

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 742 259 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:

18.10.2000 Bulletin 2000/42

(51) Int Cl.7: **C08K 5/37, C08L 57/08**

(21) Application number: **96303242.0**

(22) Date of filing: **09.05.1996**

(54) **Latent mercaptans as multi-functional additives for halogen-containing polymer compositions**

Latente Merkaptane als multifunktionelle Additive für halogenhaltige Polymerzusammensetzungen

Mercaptanes latentes comme additifs multi-fonctionnaux pour des compositions polymériques  
halogénées

(84) Designated Contracting States:

**AT BE CH DE DK ES FI FR GB GR IE IT LI LU NL  
SE**

(30) Priority: **10.05.1995 US 435413**  
**23.02.1996 US 597093**

(43) Date of publication of application:  
**13.11.1996 Bulletin 1996/46**

(73) Proprietor: **Morton International, Inc.**  
**Chicago, Illinois 60606-1596 (US)**

(72) Inventor: **Duvall, Tod C.**

**West Chester, Ohio 45069 (US)**

(74) Representative:

**Bankes, Stephen Charles Digby et al**

**BARON & WARREN**

**18 South End**

**Kensington**

**London W8 5BU (GB)**

(56) References cited:

**EP-A- 0 214 932**

**GB-A- 1 042 639**

**US-A- 3 660 331**

**US-A- 4 519 430**

**US-A- 5 109 046**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 742 259 B1**

## Description

[0001] This invention relates to stabilizer compositions comprising degradation products of a blocked mercaptan present during processing of the composition at an elevated temperature, said products including a free mercaptan. This invention also relates to polymer compositions containing a polymer normally susceptible to heat-induced deterioration and the degradation products of a blocked mercaptan present during processing of the composition at an elevated temperature, said products including a free mercaptan. It also relates to such polymer compositions further containing a metallic-based heat stabilizer. This invention also relates to articles of manufacture, e.g. pipe, film, and window profile, made from stabilized polymer compositions containing a polymer normally susceptible to heat-induced deterioration, the degradation products of blocked mercaptan present during processing of the composition at an elevated temperature, said products including a free mercaptan, and a metallic-based heat stabilizer. Another aspect of this invention is the development of a novel reaction scheme which, although crude, affords latent mercaptans which need no purification to be highly active PVC heat stabilizers at low use levels.

[0002] This invention also relates to latent mercaptans which are substantially free of the offensive odor typical of mercaptans and which may be used as anti-oxidants, odorants, anti-microbial agents, and photostabilizers; and as intermediates for the preparation of primary heat stabilizers.

[0003] It is well known that the physical properties of various organic polymers deteriorate and color changes take place during processing of the polymer and during exposure of formed polymer products to certain environments. The prime examples of polymers which are susceptible to degradation during processing are the halogen-containing polymers such as the vinyl and vinylidene polymers in which the halogen is attached directly to carbon atoms. Poly (vinyl chloride) or PVC, copolymers of vinyl chloride and vinyl acetate, and poly (vinylidene chloride), the principal resin in self-clinging transparent food wraps, are the most familiar polymers which require stabilization for their survival during fabrication into pipes, window casings, siding, bottles, and packaging film, etc. When such polymers are processed at elevated temperatures, undesirable color changes often occur within the first 5 to 10 minutes as well as during later stages of the processing. Haziness, which sometimes accompanies the color changes, is particularly undesirable where clear products are needed. The addition of heat stabilizers to such polymers has been absolutely essential to the widespread utility of the polymers. From a great deal of work in the development of more and more effective heat stabilizers there has emerged two principal classes: organotin compounds and mixed metal combinations. Organotin-based heat stabilizers are the most efficient and widely used PVC stabilizers. Synergistic combinations of alkyltin mercaptides and free mercaptans are particularly efficient heat stabilizers for PVC during extrusion. They have not been entirely satisfactory, however, because of several failings on the part of the mercaptan synergist. Many mercaptans give off an offensive odor even at room temperature and the odor grows worse at PVC processing temperatures. The oxidative stability of the mercaptans is very often very poor. Oxidation of the free mercaptans diminishes the synergism. Thus, a combination having an enhanced synergism would be welcomed by the PVC industry. Also, because of the end-use of articles made from some polymers, many polymeric compositions require the presence of both biocides and heat stabilizers but the use of the organotin mercaptide/mercaptan combination in such a composition is often frustrated by the tendency of the free mercaptan to deactivate a biocide such as the much used OBPA (10, 10'-oxybisphenoxarsine). Better heat stabilizer compositions are still needed.

[0004] GB-A-1042639 discloses a number of hydroxydialkylbenzyl compounds (including cycloalkyl and aralkyl compounds) which incorporate blocked mercaptan groups and which are useful antioxidants.

[0005] EP-A-214932 discloses the addition to lubricants, hydraulic fluids or elastomers of antioxidant compounds comprising phenols having blocked mercaptan substituents.

[0006] US-A-3660331 discloses the stabilization of vinyl halide resins with tetrahydropyranyl ethers or esters, including thioethers and thioesters.

[0007] The present invention consists in a composition comprising a halogen-containing polymer and degradation products of a blocked mercaptan present during the processing of the composition at an elevated temperature, said products including free mercaptan and the blocked mercaptan having the structure defined by general formula 1 below.

[0008] There can thus be provided a heat stabilizer composition having the synergy of a mercaptan plus improved oxidative stability. Blocking of the mercaptan group provides a latent mercaptan-containing heat stabilizer composition which is substantially free from the offensive odor typically associated with mercaptans, and can indeed provide a composition which has a decidedly pleasant odor.

[0009] The polymer composition may contain a biocide in addition to the latent mercaptan-containing heat stabilizer.

[0010] The invention further provides latent mercaptans as intermediates for the preparation of anti-oxidants, anti-microbial agents, photostabilizers, and primary heat stabilizers.

[0011] The basis of the invention is the incorporation into a polymeric composition of a blocked mercaptan which degrades during processing of the composition at an elevated temperature to liberate a free mercaptan. The latent mercaptan may act as the sole heat stabilizer but the free mercaptan may also synergize the activity of other heat stabilizers in the composition. Other products of the degradation of the blocked mercaptan are believed to include

carbocations of the blocking moiety which are stabilized by a molecular structure in which the electron deficiency is shared by several groups. Resonance stabilization and neighboring group stabilization are two of the possible mechanisms by which the carbocations may be stabilized. The carbocations act as intermediates in the formation of stable compounds early in the hot processing of halogen-containing polymers. Although such mechanisms and the resultant carbocations are believed to be an impetus for the liberation of the active free mercaptan, this invention is in no way limited by the foregoing attempt to explain the working of the invention. Those skilled in the art will see the resonance stabilization and neighboring group stabilization that are possible in the following structures of the blocked mercaptan; other mechanisms may be at work in other blocked mercaptans represented by these structures that also liberate an active free mercaptan upon thermal and/or chemical degradation during processing of polymeric compositions containing such blocked mercaptans.

[0012] The stabilizer compositions of the present invention comprise a metal-based stabilizer and such a latent mercaptan or mixture of latent mercaptans.

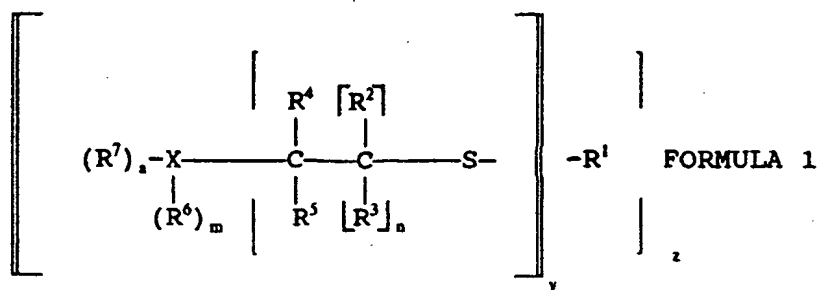
[0013] As used herein the terms alkyl, alkylene, ethylene, etc. represent monovalent and divalent, respectively, straight or branched chain hydrocarbon radicals containing, for example, 1 to 20 carbon atoms. The term aryl refers to monovalent  $C_6$ - $C_{10}$  aromatic rings such as benzene and naphthalene. The term alkenyl refers to monovalent straight or branched chain  $C_2$  to  $C_{20}$  hydrocarbon radicals containing at least one double bond. The term aralkyl represents a monovalent  $C_1$  to  $C_{20}$  hydrocarbon radical having attached thereto an aryl radical. The term alkaryl refers to monovalent aryl radicals having attached thereto at least one  $C_1$ - $C_{20}$  alkyl group. The term cycloalkyl represents monovalent  $C_3$ - $C_8$  saturated cycloaliphatic radicals, and the term cycloalkenyl represents  $C_5$ - $C_8$  cycloaliphatic radicals containing at least one double bond.

[0014] The polymeric compositions of this invention contain polymers normally susceptible to heat-induced deterioration through autoxidation such as the above-noted halogen-containing polymers. The stabilizer compositions of this invention are particularly suited to impart stabilization against the deteriorative effects of heat and ultra-violet light on halogen-containing organic polymers which is superior to that imparted by stabilizer compositions previously known in the art.

[0015] The term halogen-containing organic polymers as used herein refers to halogen-containing vinyl and vinylidene polymers or resins in which the halogen is attached directly to the carbon atoms. Preferably, the polymer is a vinyl halide polymer, more particularly a vinyl chloride polymer. Usually, the vinyl chloride polymer is made from monomers consisting of vinyl chloride alone or a mixture of monomers comprising, preferably, at least 70% by weight based on the total monomer weight of vinyl chloride.

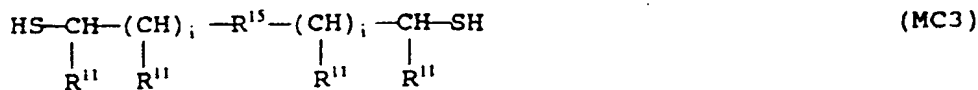
[0016] The halogen-containing polymers which can be stabilized according to this invention include chlorinated polyethylene having 14 to 75%, e.g. 27%, chlorine by weight, chlorinated natural and synthetic rubber, rubber hydrochloride, chlorinated polystyrene, chlorinated polyvinyl chloride, polyvinyl bromide, polyvinyl fluoride, copolymers of vinyl chloride with 1 to 90%, preferably 1 to 30%, of a copolymerizable ethylenically unsaturated material such as, for example, vinyl acetate, vinyl butyrate, vinyl benzoate, vinylidene chloride, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate, methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methacrylate and other alkyl methacrylates, methyl alpha-chloroacrylate, styrene, trichloroethylene, vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether and vinyl phenyl ether, vinyl ketones such as vinyl methyl ketone and vinyl phenyl ketone, 1-fluoro-2-chloroethylene, acrylonitrile, chloroacrylonitrile, allylidene diacetate and chloroallylidene diacetate. Typical copolymers include vinyl chloride-vinyl acetate (96:4 sold commercially as VYNW), vinyl chloride-vinyl acetate (87:13), vinyl chloride-vinyl acetate-maleic anhydride ((86:13:1), vinyl chloride-vinylidene chloride (95:5); vinyl chloride-diethyl fumarate (95:5), and vinyl chloride 2-ethylhexyl acrylate (80:20). In addition to the stabilizer compositions of this invention, there can also be incorporated into the halogen-containing organic polymer conventional additives such as plasticizers, pigments, fillers, dyes, ultra-violet light absorbing agents, densifying agents, biocides and the like.

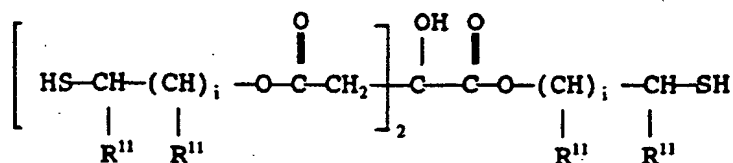
[0017] FORMULA 1 is representative of the blocked mercaptans that are used in the compositions of this invention:



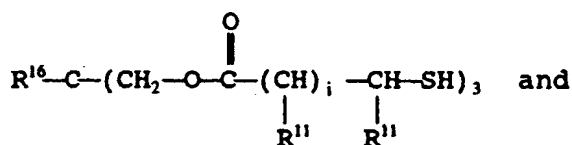
wherein a is 0 or 1, m and n are 0 or 1; y = 1 to 4, z is 1 to 4 when y is 1 and z is 1 when y is more than 1; R<sup>1</sup> is a tetrahydropyranyloxyethyl group or a hydroxyalkyl, carboxyalkyl, carboxyaryl, or carboxyaryl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently hydrogen, a hydroxyl or mercapto group or an alkyl, alkylenyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxyhydroxyaryl, mercaptoaryl or acyl group having from 1 to 22 carbon atoms; X is aryl, haloaryl, alkaryl, aralkyl, alkoxyaryl, arylcycloalkyl, or a heteroatom, with the proviso that when a is 1 and m is 1, R<sup>6</sup> and R<sup>7</sup> may form a heterocyclic moiety in conjunction with X as a nitrogen atom, and when a = 1 and m = 0, one of R<sup>1</sup>, R<sup>3</sup>, and R<sup>5</sup> may join with R<sup>7</sup> and X as to form a heterocyclic moiety with X as a heteroatom of oxygen or sulfur, with the further proviso that when X is aralkaryl, R<sup>6</sup> and R<sup>7</sup> are hydroxyl, a is 1 and m is 1, then z is 1 or 2, and with the still further proviso that when R<sup>6</sup> ≠ hydroxyl or mercapto, z is 1.

[0018] The mercaptan-containing organic compounds which may be converted into latent mercaptans for the purposes of this invention are well-known compounds and include alkyl mercaptans, mercapto esters, mercapto alcohols, and mercapto acids. See, for example, U.S. Pat. Nos. 3,503,924 and 3,507,827. Alkyl mercaptans having from 1 to about 200 carbon atoms and from 1 to 4 mercapto groups are suitable. Mercaptan-containing organic compounds which include R<sup>1</sup> have structures illustrated by the following formulas:

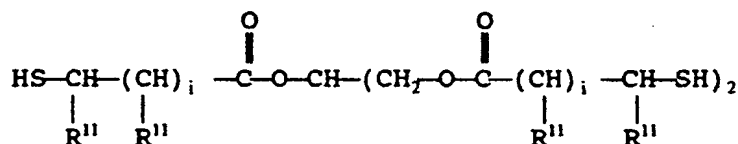




(MC4)

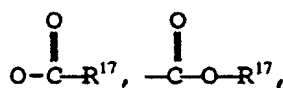
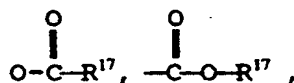


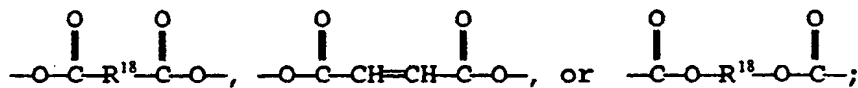
(MC5)



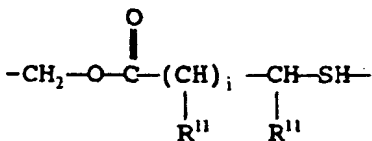
(MC6)

wherein

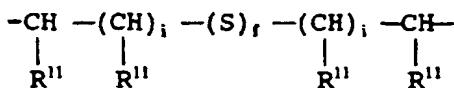
R<sup>10</sup> and R<sup>19</sup> are the same or different and are-OH, -SH, aryl, C<sub>1</sub> to C<sub>18</sub> alkyl, or -H;R<sup>11</sup> is -H, aryl, or C<sub>1</sub> to C<sub>18</sub> alkyl;R<sup>12</sup> is cycloalkyl, cycloalkenyl or phenyl;R<sup>13</sup> is-SH, aryl, C<sub>1</sub> to C<sub>18</sub> alkyl, -OH or -H with the proviso that in formula (MC2) when R<sup>12</sup> is phenyl, R<sup>13</sup> is -OH and i=0, then the -SH groups are on non-adjacent carbon atoms;R<sup>14</sup> is -H or a divalent group which may contain halogen, hydroxy, mercapto or alkyl substituents and which when R<sup>12</sup> is phenyl combines with the phenyl to form a naphthalene ring;R<sup>15</sup> is



R<sup>16</sup> is -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, or



R<sup>17</sup> is -H, or alkyl, alkenyl, aryl, aralkyl, alkaryl, cycloalkyl, cycloalkylenyl;  
R<sup>18</sup> is arylene, C<sub>1</sub> to C<sub>8</sub> alkylene,



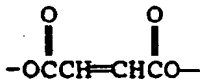
or -(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>b</sub>-CH<sub>2</sub>-CH<sub>2</sub>-

wherein b is an integer from 1 to 6;  
i=0 or an integer from 1 to 6 inclusive;  
j=0, 1, 2 or 3; and  
f=1 or 2.

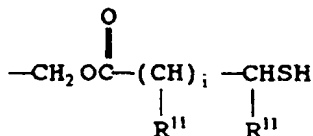
[0019] Mercaptan-containing organic compounds preferred as intermediates in the preparation of the latent mercaptans of this invention are those compounds according to formula (MC1) where R<sup>11</sup> is -H, R<sup>19</sup> is -H, R<sup>10</sup> is OH or



and i=1; those compounds according to formula (MC2) where R<sup>12</sup> is phenyl, R<sup>11</sup> is -H, R<sup>13</sup> is -H, R<sup>14</sup> is -H, i=1, and j=1; those compounds according to formula (MC3) where R<sup>11</sup> is -H, R<sup>15</sup> is



and i=1; those compounds according to formula (MC4) where R<sup>11</sup> is -H and i=1; those compounds according to formula (MC5) where R<sup>16</sup> is -C<sub>2</sub>H<sub>5</sub> or

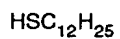


EP 0 742 259 B1

R<sup>11</sup> is -H and i=1; and those compounds according to formula (MC6) where R<sup>11</sup> is -H and i=1.

[0020] Examples of the mercaptan-containing organic compounds described by formula (MC1) include, but are not limited to, the following compounds:

5



10

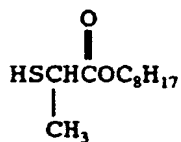


15



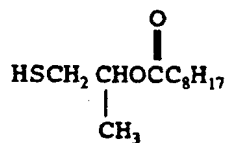
20

25



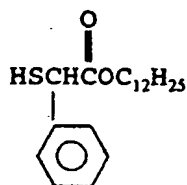
30

35



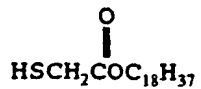
40

45



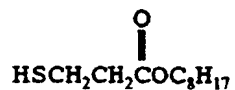
50

55

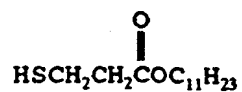


EP 0 742 259 B1

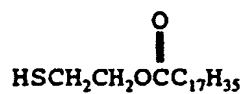
5



10

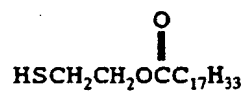


15

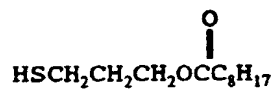


20

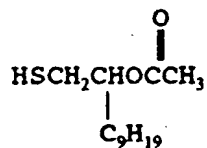
25



30

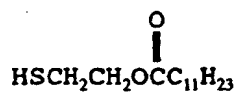


35



40

45



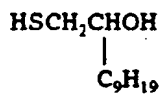
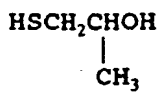
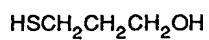
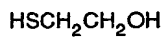
50

55

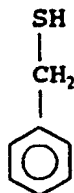
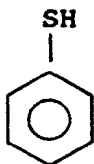




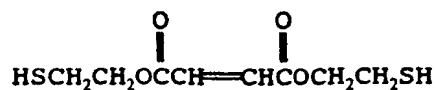
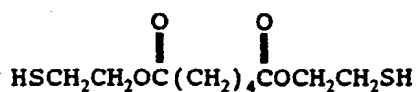
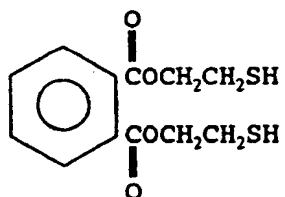
EP 0 742 259 B1



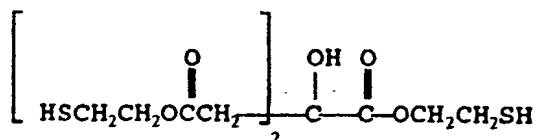
[0021] Examples of the mercaptan-containing organic compounds described by formula (MC2) include, but are not limited to, the following compounds:



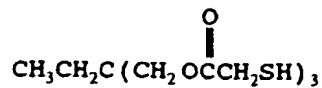
[0022] Examples of mercaptan-containing organic compounds represented by formula (MC3) include, but are not limited to the following compounds:



[0023] The mercaptan-containing organic compounds described by formula (MC4) are exemplified by, but are not limited to, the following:

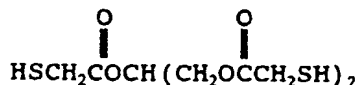
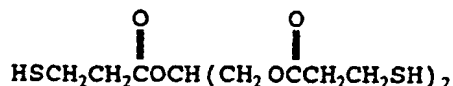


[0024] The mercaptan-containing organic compounds represented by formula (MC5) are exemplified by, but are not limited to, the following:



[0025] The mercaptan-containing organic compounds represented by formula (MC6) are exemplified by, but are not

limited to, the following:



[0026] One of the advantages of this invention is that the offensive odor of the mercaptans is masked by the blocking group so that the latent mercaptan thus created may be put into a PVC composition or the like with little or no offense to the operator with the knowledge that the free mercaptan will be released as a degradation product when the treated composition is heated during the usual processing, e.g. extrusion. This advantage is also useful for the liquid polysulfides having a molecular weight of from about 1000 to about 8000 sold under the LP trademark by Morton International, Inc.

[0027] The blocking compounds are preferably those which are capable of furnishing a stabilized carbocation having a molecular structure in which the electron deficiency is shared by several groups. Resonance stabilization and neighboring group stabilization are two of the possible mechanisms by which the carbocations may be stabilized. Polarized, unsaturated compounds exemplified by 3,4-dihydropyran, 2-methoxy-3,4-dihydropyran, styrene,  $\alpha$ -methylstyrene, vinyl benzyl chloride, indene, 2-vinylpyridine, N-vinylpyrrolidone, vinyl acetate, octadecyl vinyl ether, cyclohexyl divinyl ether, ethyleneglycol monovinyl ether, allyl phenyl ether, trans-cinnamaldehyde, N-methyl-N-vinylacetamide, N-vinylcaprolactam, isoeugenol, and 2-propenylphenol are suitable. Compounds having labile halogen atoms which split off as hydrogen chloride in a condensation reaction with the mercaptan, as exemplified by triphenylmethyl chloride, benzyl chloride, and bis(chloromethyl)benzene, are also suitable. The mercaptan may also be blocked by condensation with an aldehyde such as butyraldehyde or with a benzyl alcohol such as benzene dimethanol. A preferred blocking agent is 2-hydroxybenzyl alcohol, a well known intermediate in the perfume, agricultural, and plastics industries.

[0028] In general, the procedure for adding the mercapto group of a free mercaptan across the double bonds of polarized, unsaturated compounds is:

[0029] To a stirred mixture of the mercaptan, acid catalyst, and optionally, a small percentage of antioxidant to inhibit radical reactions, under nitrogen atmosphere is added dropwise the polarized, unsaturated compound, either neat or in solution, while maintaining the temperature between 10°-70° C. The mixture or solution is then heated for between 1 to 6 hours at 35°-70° C and conversion to product is monitored by gas chromatography and iodine titration for SH. The acid catalyst is removed by an alkaline wash and the resulting product is dried with magnesium sulfate and filtered. The solvent, if required, is removed under reduced pressure at <50° C to yield the latent mercaptan. This generalized procedure is referred to hereinafter as Procedure A.

[0030] In accordance with Procedure A, for example, mercaptoethanol is added across the double bond of N-vinylcaprolactam to yield N-2-hydroxyethylthioethylcaprolactam. Mercaptoethylcaprate reacts with 3,4-dihydropyran in that procedure to give 2-(2-caproyloxyethyl)tetrahydropyran. Bis(hydroxyethylthioethyl) cyclohexyl ether is made from the mercaptoethanol and cyclohexyl di-vinyl ether. In like manner, the corresponding caprate, oleate, and tallate esters form the corresponding cyclohexyl ethers. Also, indene is converted by the addition of the mercaptoethanol to 2H-dihydroindenythio-ethanol.

[0031] A generalized procedure for the condensation of a free mercaptan with a labile halogen-containing compound is as follows:

[0032] To a stirred mixture of the mercaptan and halogen-containing compound under nitrogen atmosphere is added dropwise a solution of sodium methoxide in methanol while maintaining the temperature below 50° C. Optionally, the reaction is allowed to proceed without the addition of a base source and the liberated hydrogen chloride is removed by nitrogen gas sweep and neutralized with the use of an external acid scrubber. The mixture or solution is then heated for between 2 to 24 hours at 50°-70° C and conversion to product is monitored by gas chromatography and iodine titration for %SH. The product is then neutralized, washed with water, dried with magnesium sulfate, and filtered. The solvent, if required, is removed under reduced pressure at <50° C to yield the latent mercaptan. This generalized procedure is referred to hereinafter as Procedure B.

[0033] A generalized procedure for the condensation of a free mercaptan with a labile hydroxyl-containing compound

is as follows: To a stirred solution of the mercaptan, acid catalyst, and solvent under nitrogen atmosphere is added the hydroxy-containing compound either neat or in solution while maintaining the temperature  $<45^{\circ}\text{C}$ . The solution is then heated to  $45^{\circ}\text{--}75^{\circ}\text{C}$  for between 1 to 10 hours and conversion to product is monitored by gas chromatography and iodine titration for %SH. Optionally, an azeotropic solvent is chosen for removal of reaction water by an appropriate means at reflux temperatures, typically  $60^{\circ}\text{--}120^{\circ}\text{C}$ . Completion of reaction is achieved after the theory amount of water has been collected. The acid catalyst is removed by alkaline wash and the resulting solution is dried with magnesium sulfate and filtered. The solvent is removed under reduced pressure at  $<55^{\circ}\text{C}$  to yield the latent mercaptan. This procedure is referred to hereinafter as Procedure C.

[0034] For example, 2-hydroxybenzyl alcohol condenses with mercaptoethanol in accordance with Procedure C to form 1-(2-hydroxyphenyl)-1-S-(2-hydroxyethanethio)methane.

[0035] A generalized procedure for the reaction of a free mercaptan with a glycidyl ether is as follows:

[0036] To a stirred mixture of the mercaptan and acid catalyst under nitrogen atmosphere is added the glycidyl ether, either neat or in solution, while maintaining the temperature between  $25^{\circ}\text{--}60^{\circ}\text{C}$ . The mixture or solution is then heated to between  $50^{\circ}\text{--}75^{\circ}\text{C}$  for a period of 1 to 6 hours and conversion to product is monitored by gas chromatography and iodine titration for %SH. The acid catalyst is removed by alkaline wash, the resulting product is dried with magnesium sulfate, and filtered. The solvent, if required, is removed under reduced pressure at  $<55^{\circ}\text{C}$  to yield the latent mercaptan. This procedure is referred to hereinafter as Procedure D.

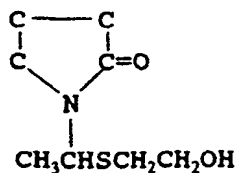
[0037] A generalized procedure for the condensation of a free mercaptan with an aldehyde is as follows:

[0038] To a stirred solution of the mercaptan, acid catalyst, and azeotropic solvent under nitrogen atmosphere is added the aldehyde with heating to reflux, typically between  $65^{\circ}\text{--}120^{\circ}\text{C}$ , for removal of reaction water. Completion of reaction is achieved after the theory amount of water has been collected. Optionally, to a stirred solution of mercaptan, aldehyde, and ether is added  $\text{BF}_3$ -etherate dropwise under reflux conditions. The solution is refluxed for between 1 to 6 hours and conversion to product is monitored by gas chromatography. The acid catalyst is removed by alkaline wash, the solution is dried with magnesium sulfate and filtered. The solvent is removed under reduced pressure at  $<65^{\circ}\text{C}$  to yield the latent mercaptan. This generalized procedure is referred to hereinafter as Procedure E.

[0039] Examples of the blocked mercaptans of this invention include compounds having the following formulas, as each relates to FORMULA 1:

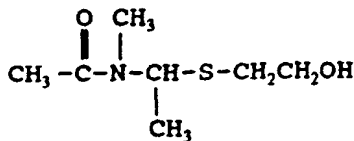
### FORMULA

2.



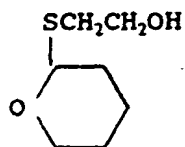
$a = 1, m = 1, n = 0; y = 1, z = 1; X$  is nitrogen,  $R^6$  and  $R^7$  are joined to form  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-$ ;  $R^4$  is hydrogen;  $R^5$  is methyl; and  $R^1$  is hydroxyethyl.

3.



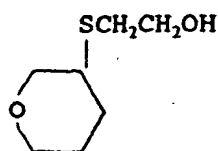
$a = 1, m = 1, n = 0; y = 1, z = 1; X$  is nitrogen,  $R^6$  is acetyl,  $R^7$  is methyl,  $R^5$  is methyl,  $R^4$  is hydrogen, and  $R^1$  is hydroxyethyl.

4.



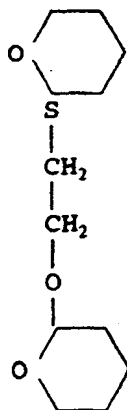
a = 1, m = 0, n = 0; y = 1, z = 1; X is oxygen, R<sup>5</sup> and R<sup>7</sup> are joined to form -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>4</sup> is hydrogen, and R<sup>1</sup> is hydroxyethyl.

5.



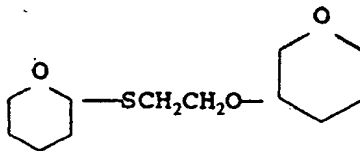
a = 1, m = 0, n = 1, y = 1, z = 1; X is oxygen, R<sup>3</sup> and R<sup>7</sup> join to form -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>2</sup>, R<sup>4</sup> and R<sup>5</sup> are hydrogen, and R<sup>1</sup> is hydroxyethyl.

6.



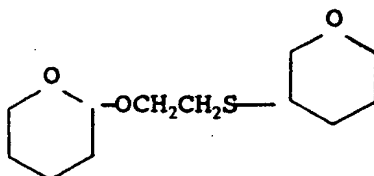
a = 1, m = 0, n = 0, y = 1, z = 1; X is oxygen, R<sup>5</sup> and R<sup>7</sup> join to form -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>4</sup> is hydrogen, and R<sup>1</sup> is tetrahydropyranyloxyethyl

7.



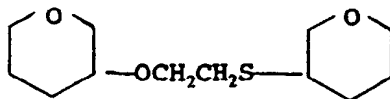
a = 1, m = 0, n = 0, y = 1, z = 1; X is oxygen, R<sup>5</sup> and R<sup>7</sup> join to form -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>4</sup> is hydrogen, and R<sup>1</sup> is tetrahydropyranyloxyethyl.

8.



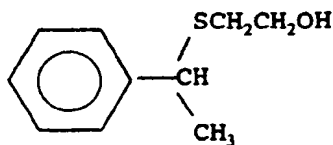
a = 1, m = 0, n = 1, y = 1, z = 1; X is oxygen, R<sup>3</sup> and R<sup>7</sup> join to form -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>2</sup>, R<sup>4</sup> and R<sup>5</sup> are hydrogen, and R<sup>1</sup> is tetrahydropyranyloxyethyl

9.



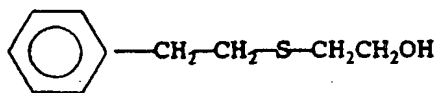
a = 1, m = 0, n = 1, y = 1, z = 1; X is oxygen, R<sup>3</sup> and R<sup>7</sup> join to form -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>2</sup>, R<sup>4</sup> and R<sup>5</sup> are hydrogen, and R<sup>1</sup> is tetrahydropyranyloxyethyl

10a.



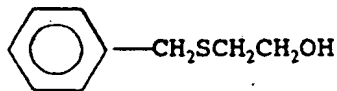
a = 0, m = 0, n = 0, y = 1, z = 1; X is phenyl, R<sup>4</sup> is methyl, R<sup>5</sup> is hydrogen, and R<sup>1</sup> is hydroxyethyl.

10b.



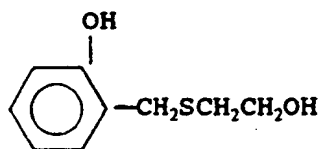
a = 0, m = 0, n = 1, y = 1, z = 1, X is phenyl, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are hydrogen, and R<sup>1</sup> is hydroxyethyl.

11.



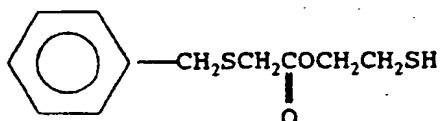
a = 0, m = 0, n = 0, z = 1; y = 1, X is phenyl, R<sup>4</sup> and R<sup>5</sup> are hydrogen, and R<sup>1</sup> is hydroxyethyl.

12.



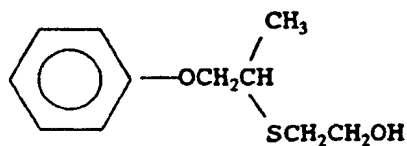
a = 1, m = 0, n = 0, y = 1, z = 1; X is phenyl, R<sup>4</sup> and R<sup>5</sup> are hydrogen, R<sup>7</sup> is o-hydroxy, and R<sup>1</sup> is hydroxyethyl.

13.



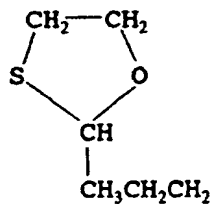
a = 0, m = 0, n = 0, y = 1, z = 1; X is phenyl, R<sup>4</sup> and R<sup>5</sup> are hydrogen, and R<sup>1</sup> is mercaptoethoxycarbonylmethyl.

14.



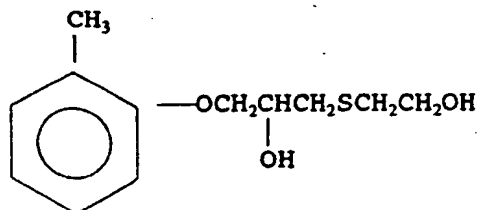
a = 1, m = 0, n = 1, y = 1, z = 1; X is oxygen, R<sup>2</sup>, R<sup>4</sup> and R<sup>5</sup> are hydrogen, R<sup>3</sup> is methyl, R<sup>7</sup> is phenyl, and R<sup>1</sup> is hydroxyethyl.

15.



a = 1, m = 0, n = 0, y = 1, z = 1; X is oxygen, R<sup>7</sup> and R<sup>1</sup> are joined to form an ethylenyl radical, R<sup>4</sup> is hydrogen, and R<sup>5</sup> is propyl.

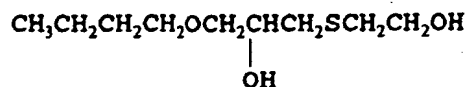
16.



EP 0 742 259 B1

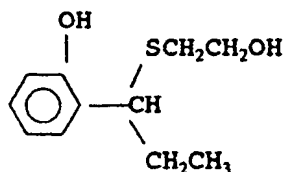
$a = 0, m = 1, n = 1, y = 1, z = 1$ ; X is oxygen,  $R^2, R^3, R^6$  and  $R^4$  are hydrogen,  $R^5$  is 2-methyleneoxytolyl.

17.



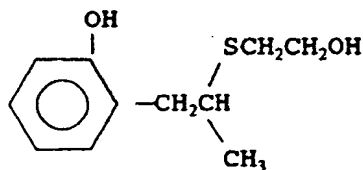
$a = 1, m = 0, n = 1, y = 1, z = 1$ ; X is oxygen,  $R^2, R^3, R^4$  and  $R^7$  are hydrogen,  $R^5$  is butoxymethylenyl.

18.



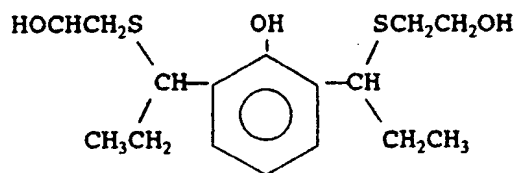
$a = 1, m = 0, n = 0, y = 1, z = 1$ ; X is phenyl,  $R^4$  is hydrogen,  $R^5$  is ethyl,  $R^7$  is *o*-hydroxy, and  $R^1$  is hydroxyethyl.

19.



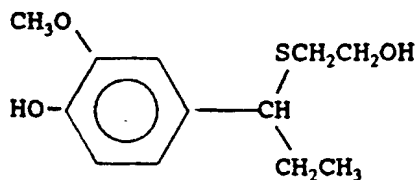
$a = 1, m = 0, n = 1, y = 1, z = 1$ ; X is phenyl,  $R^3, R^4$  and  $R^5$  are hydrogen,  $R^2$  is methyl,  $R^7$  is *o*-hydroxy, and  $R^1$  is hydroxyethyl.

20.



$a = 1, m = 0, n = 0, y = 1, z = 2$ ; X is phenyl,  $R^4$  is hydrogen,  $R^5$  is ethyl,  $R^7$  is *o*-hydroxy, and  $R^1$  is hydroxyethyl.

21.

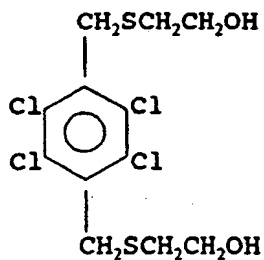




EP 0 742 259 B1

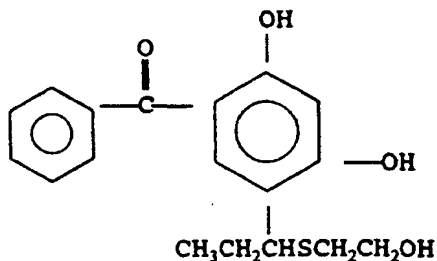
$a = 1, m = 0, n = 0, y = 1, z = 1$ ; X is m-methoxyphenyl,  $R^4$  is hydrogen,  $R^5$  is ethyl,  $R^7$  is *p*-hydroxy, and  $R^1$  is hydroxyethyl.

22.



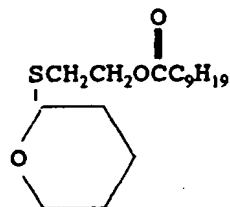
$a = 0, m = 0, n = 0, y = 1, z = 2$ ; X is tetrachlorophenyl,  $R^4$  and  $R^5$  are hydrogen, and  $R^1$  is hydroxyethyl.

23.



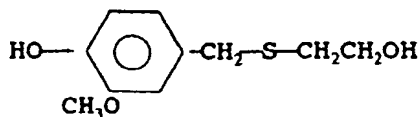
$a = 1, m = 0, n = 0, y = 1, z = 1$ ; X is o,p-dihydroxyphenyl,  $R^7$  is m-phenylcarbonyl,  $R^4$  is hydrogen,  $R^5$  is  $-\text{CH}_2\text{CH}_3$ , and  $R^1$  is hydroxyethyl.

24.



$a = 1, m = 0, n = 0, y = 1, z = 1$ ; X is oxygen,  $R^5$  and  $R^7$  are joined to form  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ;  $R^4$  is hydrogen, and  $R^1$  is caproyloxyethyl.

25.



$a = 1, m = 0, n = 0, y = 1, z = 1$ ; X is *p*-hydroxyphenyl,  $R^4$  and  $R^5$  are hydrogen,  $R^7$  is m-methoxy, and  $R^1$  is hydroxyethyl.

[0040] As stated above, the stabilizer compositions of the present invention comprise a latent mercaptan as the sole heat stabilizer or in a system comprising a metal-based stabilizer, an organic-based stabilizer, or a hydrotalcite-based stabilizer in admixture with the latent mercaptan. Metal-based stabilizers are defined for the purposes of this invention as metal salt stabilizers and organometallic stabilizers. The metal salt stabilizers are exemplified by barium, strontium, calcium, cadmium, zinc, lead, tin, magnesium, cobalt, nickel, titanium, antimony, and aluminum salts of phenols, aromatic carboxylic acids, fatty acids, epoxidized fatty acids, oxalic acid, carbonic acid, sulfuric acid, and phosphoric acid. Calcium stearate, calcium 2-ethylhexeate, calcium octoate, calcium oleate, calcium ricinoleate, calcium myristate, calcium palmitate, calcium laurate, barium laurate, barium stearate, barium di(nonylphenolate), magnesium stearate, zinc stearate, cadmium laurate, cadmium octoate, cadmium stearate, sodium stearate and other Group I and II metal soaps are examples of suitable salts. Other metal salts such as lead stearate, hydrotalcite, aluminum stearate, etc, can be used. Metal salt stabilizers may constitute from about 0.1 to about 10%, preferably 0.1-5% by weight of the halogen containing resin.

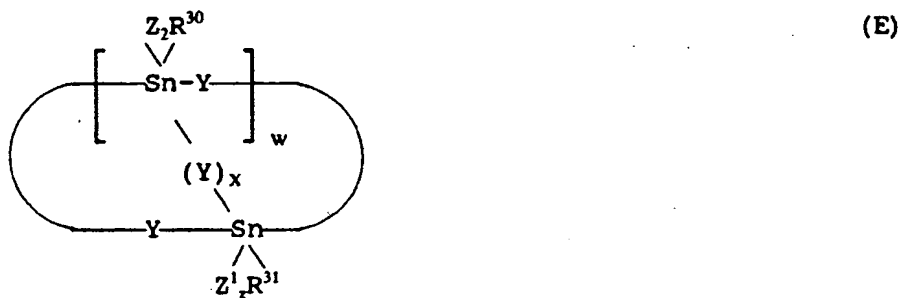
[0041] Conventional organometallic stabilizers include the organotin carboxylates and mercaptides. Such materials include butyltin tris dodecyl mercaptide, dibutyltin dilaurate, dibutyltin didodecyl mercaptide, dianhydride tris dibutyls-tannane diol, dihydrocarbotin salts of carboxy mercaptals such as those set forth in Hechenbleikner et al.(U.S. Pat. No. 3,078,290). There can be included any of the vinyl chloride resin stabilizers set forth in Salyer (U.S. Pat. No. 2,985,617).

[0042] As an example of a system involving an organic-based stabilizer, a combination of a latent mercaptan and an N-substituted maleimide has been found to be synergistic in the stabilization of a flexible PVC formulation.

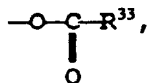
[0043] The stabilizer compositions of this invention comprise from about 10% to about 100%, preferably from about 35% to about 85%, by weight of one or more latent mercaptans, based on the total weight of the stabilizer composition, the balance comprising the metal-based, organic-based, or hydrotalcite-based stabilizer. Preferably, the stabilizer compositions of this invention comprise a mono-organotin compound or mixture of mono-organotin compounds, and, optionally, a diorganotin compound or mixture of diorganotin compounds or mixtures of mono-organotin and diorganotin compounds. Thus, when no diorganotin compound or mixture of diorganotin compounds is employed in the preferred stabilizer of this invention, the mono-organotin compounds will comprise from about 10% to about 90% by weight, preferably about 15% to about 65% by weight of the total weight of the stabilizer composition. When it is desirable to utilize a diorganotin compound or mixture of diorganotin compounds in the practice of this invention, said diorganotin compound or mixture of diorganotin compounds may comprise from about 0.05% to about 75%, by weight, preferably from about 0.05% to about 35% by weight of the total weight of the stabilizer composition.

[0044] The mono-organotin compounds useful in the compositions of this invention contain one or more tetravalent tin atoms each of which have one direct tin to carbon bond and have structures selected from the following formulas:

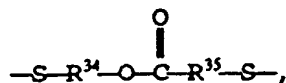
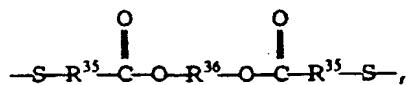
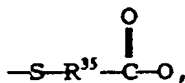
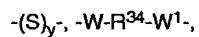


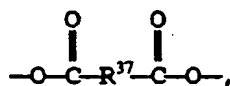
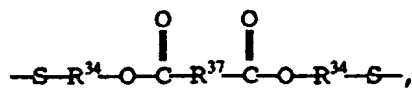


wherein Z and Z' are the same or different and are selected from -SR<sup>32</sup>, O-R<sup>33</sup>, and

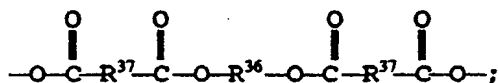


with the proviso that in formula (E) when z = 1 and in formulas (C) and (D) at least one Z or Z' is -SR<sup>32</sup>; Y is

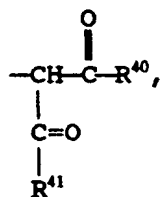
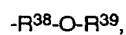
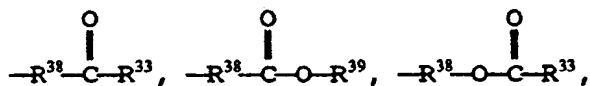




or

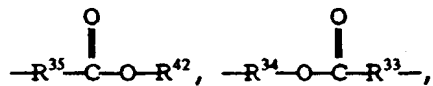


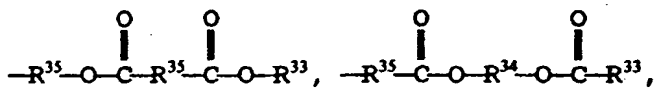
W and W<sup>1</sup> are the same or different and are oxygen or sulfur; R<sup>30</sup> and R<sup>31</sup> are the same or different and are selected from alkyl, aryl, alkenyl, aralkyl, alkaryl, cycloalkyl, cycloalkenyl,



and, -R<sup>38</sup>-CN;

R<sup>32</sup> is alkyl, alkenyl, aryl, aralkyl, cycloalkyl, cycloalkenyl,





---R<sup>34</sup>-S-R<sup>42</sup>, or -R<sup>34</sup>-O-R<sup>33</sup>;

R<sup>33</sup> is alkyl, alkenyl, aryl, aralkyl, alkaryl, cycloalkyl, or cycloalkenyl;

R<sup>34</sup> is alkylene of at least 2 carbon atoms, arylene, alkenylene of at least 2 carbon atoms, cycloalkylene, or cycloalkenylene;

R<sup>35</sup> is alkylene, arylene, alkenylene of at least 2 carbon atoms, cycloalkylene, or cycloalkenylene;

R<sup>36</sup> is R<sup>34</sup>;

R<sup>37</sup> is nothing or R<sup>35</sup>;

R<sup>38</sup> is C<sub>1</sub> to C<sub>4</sub> alkylene;

R<sup>39</sup> is -H or a monovalent C<sub>1</sub> to C<sub>20</sub> hydrocarbon radical;

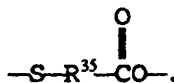
R<sup>40</sup> and R<sup>41</sup> are the same or different and are each C<sub>1</sub> to C<sub>22</sub> alkyl or C<sub>1</sub> to C<sub>20</sub> alkoxy;

R<sup>42</sup> is -H or R<sup>33</sup>;

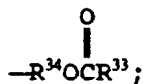
q = 0 or an integer from 1 to 4 inclusive;

v = an integer from 1 to 8 inclusive; and

w = 0, 1 or 2, x = 0 or 1, z = 0 or 1 with the proviso that when x = 0 then z = 1, when x = 1 then z = 0 and w = 1, when w = 2 then x = 0 and z = 1, and when w = 0 then x = 0, z = 1 and Y is -W-R<sup>34</sup>-W<sup>1</sup>- or



[0045] The preferred mono-organotin compounds useful in this invention are those compounds according to formula (A) where R<sup>30</sup> is methyl, butyl or octyl and W is sulfur; those compounds according to formula (B) where R<sup>31</sup> is methyl or butyl, W is sulfur, Z is -SR<sup>32</sup> where R<sup>32</sup> is



those compounds according to formula (C) where R<sup>30</sup> is methyl or butyl, Z is -SR<sup>32</sup> where R<sup>32</sup> is



those compounds according to formula (D) where R<sup>30</sup> is methyl, Z is -SR<sup>32</sup> where R<sup>32</sup> is



R<sup>31</sup> is methyl, Z' is -SR<sup>32</sup> where R<sup>32</sup> is



Y is -S-, and q = 0; and those compounds according to formula (E) where R<sup>30</sup> is methyl, Z is -SR<sup>32</sup> where R<sup>32</sup> is



R<sup>31</sup> is methyl, Z' is -SR<sup>32</sup> where R<sup>32</sup> is



Y is -S-, W=1, x = 0, and z = 1.

[0046] Examples of mono-organotin compounds which are useful in this invention include, but are not limited to, those illustrated in Tables 1-4 below. Thus, representative of the mono-organotin compounds described by formulas (A) and (B) are those illustrated in Table 1 below.

TABLE 1

(A) $\left[ \begin{array}{c} R^{30}-Sn \\   \\ W \end{array} \right]_2$		(B) $\begin{array}{c} R^{31}-Sn-Z \\   \\ W \end{array}$		
Mono-organotin Compound No.	$R^{30}$	$R^{31}$	W	Z
1	$-C_4H_9$	-	S	-
2	$-C_8H_{17}$	-	O	-
3	-	$-CH_3$	S	$\begin{array}{c} O \\   \\ -SCH_2CH_2OCC_{17}H_{33} \end{array}$
4	-	$-CH_3$	S	$\begin{array}{c} O \\   \\ -SCH_2COC_8H_{17} \end{array}$
5	-	$\begin{array}{c} O \\   \\ -CH_2CH_2COC_4H_9 \end{array}$	S	$\begin{array}{c} O \\   \\ -SCH_2CH_2COC_{18}H_{37} \end{array}$

[0047] Examples of mono-organotin compounds represented by formula (C) are illustrated in Table 2 below.

TABLE 2

$R^{30}-Sn-Z_3$		(C)
Mono-organotin Compound No.	$R^{30}$	Z
6	$-CH_3$	$\begin{array}{c} O \\   \\ -SCH_2COC_8H_{17} \end{array}$
7	$-C_4H_9$	$\begin{array}{c} O \\   \\ -SCH_2CH_2OCC_7H_{15} \end{array}$

[0048] The mono-organotin compounds illustrated in Table 3 below are representative of compounds described in formula (D).

TABLE 3

5

10

15

20

25

30

35

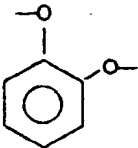
40

45

50

55

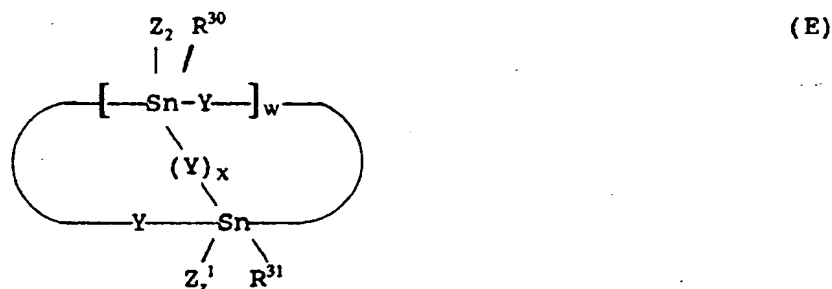
$$\begin{array}{c}
 \text{Z} \quad \text{R}^{31} \quad \text{Z} \\
 | \quad | \quad | \\
 \text{R}^{30}-\text{Sn}-\text{Y}-(\text{Sn}-\text{Y})_4-\text{Sn}-\text{R}^{30} \\
 | \quad | \quad | \\
 \text{Z}^1 \quad \text{Z} \quad \text{Z}^1
 \end{array}$$
  
(D)

Mono-organotin Compound No.	R <sup>30</sup> and R <sup>31</sup>	Z	Z <sup>1</sup>	Y	α
8	-CH <sub>3</sub>	$  \begin{array}{c}  \text{O} \\     \\  -\text{SCH}_2\text{CH}_2\text{OCC}_{11}\text{H}_{23}  \end{array}  $	Same as Z	-S-	0
9	$  \begin{array}{c}  \text{O} \\     \\  -\text{CH}_2\text{CH}_2\text{COC}_4\text{H}_9  \end{array}  $	$  \begin{array}{c}  \text{O} \\     \\  -\text{SCH}_2\text{CH}_2\text{COC}_8\text{H}_{17}  \end{array}  $	Same as Z	-S-S-	0
10	-CH <sub>3</sub>	$  \begin{array}{c}  \text{O} \\     \\  -\text{SCH}_2\text{CH}_2\text{OCC}_{17}\text{H}_{33}  \end{array}  $	Same as Z	$  \begin{array}{c}  \text{O} \quad \text{O} \\     \quad    \\  -\text{SCH}_2\text{COC}_4\text{H}_8\text{OCCH}_2\text{S}-  \end{array}  $	1
11	-CH <sub>3</sub>	$  \begin{array}{c}  \text{O} \quad \text{O} \\     \quad    \\  -\text{SCH}_2\text{CH}_2\text{OCCH}=\text{CHCOCH}_3  \end{array}  $	Same as Z	-S-	0
12	-C <sub>4</sub> H <sub>9</sub>	$  \begin{array}{c}  \text{O} \\     \\  -\text{SCH}_2\text{CH}_2\text{OCC}_8\text{H}_{17}  \end{array}  $	Same as Z	$  \begin{array}{c}  \text{O} \\     \\  -\text{S}-\text{CH}_2\text{CO}-  \end{array}  $	0
13	-CH <sub>3</sub>	$  \begin{array}{c}  \text{O} \\     \\  -\text{SCH}_2\text{CH}_2\text{OCC}_{11}\text{H}_{23}  \end{array}  $	Same as Z	-S-	0
14	-C <sub>4</sub> H <sub>9</sub>	$  \begin{array}{c}  \text{O} \\     \\  -\text{SCH}_2\text{CH}_2\text{OCC}_7\text{H}_{15}  \end{array}  $	Same as Z		0

[0049] The mono-organotin compound illustrated in Table 4 below is representative of compounds described by formula (E).



TABLE 4



## Mono-organotin

Compound No.	R <sup>30</sup> and R <sup>31</sup>	Z and Z <sup>1</sup>	Y	w	x	z
15	-CH <sub>3</sub>		-S-	1	0	1

[0050] As used in Tables 1-3 above, and throughout this specification, the radicals -C<sub>4</sub>H<sub>9</sub>, -C<sub>8</sub>H<sub>17</sub>, -C<sub>12</sub>H<sub>25</sub>, -C<sub>9</sub>H<sub>19</sub> and -C<sub>10</sub>H<sub>21</sub> represent n-butyl, n-octyl, n-dodecyl, n-nonyl and n-decyl respectively.

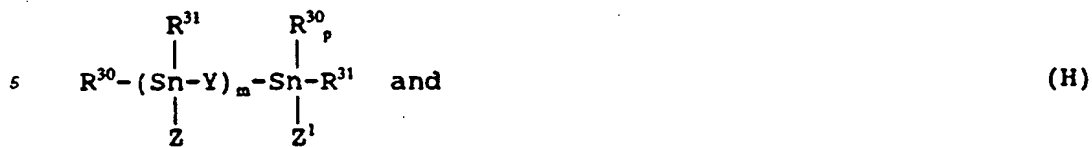
[0051] The carboxyl radicals



are derived from oleic acid, stearic acid, n-octanoic acid, lauric acid, and pelargonic acid respectively. Likewise, the radicals -OC<sub>13</sub>H<sub>27</sub>, -OC<sub>18</sub>H<sub>37</sub>, and -OC<sub>8</sub>H<sub>17</sub>, are derived from tridecanol, stearyl alcohol and iso-octanol, respectively.

[0052] The diorganotin compounds useful in the practice of this invention contain one or more tetravalent tin atoms, at least one of which has direct bonds to two carbon atoms and have structure selected from the following formulas:





20 wherein  $\text{R}^{30}$ ,  $\text{R}^{31}$ ,  $\text{W}$ ,  $\text{Z}$ ,  $\text{Z}^1$ ,  $\text{Y}$ ,  $w$  and  $z$  are as previously defined;  $n=0, 1$  or  $2$ ,  $p=0, 1$  or  $2$  with proviso that  $n+p=2$ , and  $m=1$  to  $5$ ;  
 $y=1$  or  $2$ ,  $y=2$  with the proviso that when  $w=0$  then  $\text{Y}$  is  $-\text{W}-\text{R}^{34}-\text{W}^1-$ , or



30 and in formula (J) when  $z=1$  and in formulas (G) and (H) at least one  $\text{Z}$  or  $\text{Z}^1$  is  $-\text{SR}^{32}$ .

[0053] The preferred diorganotin compounds used in the practice of this invention are those compounds according to formula (F) where  $\text{R}$  is methyl or butyl,  $\text{R}^{31}$  is methyl or butyl and  $\text{W}$  is sulfur; those compounds according to formula (G) where  $\text{R}$  is methyl or butyl,  $\text{R}^{31}$  is methyl or butyl,  $\text{Z}$  is  $-\text{SR}^{32}$  where  $\text{R}^{32}$  is



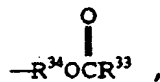
40 and  $\text{Z}^1$  is  $-\text{SR}^{32}$  is



50 those compounds according to formula (H) where  $\text{R}^{30}$  is methyl or butyl,  $\text{R}^{31}$  is methyl or butyl,  $\text{Y}$  is  $-\text{S}-$ ,  $\text{Z}$  is  $-\text{SR}^{32}$  where  $\text{R}^{32}$  is



$\text{Z}^1$  is  $-\text{SR}^{32}$  where  $\text{R}^{32}$  is



m = 1, n = 2 and p = 0; and those compounds according to formula (J) where R<sup>30</sup> is methyl or butyl, R<sup>31</sup> is methyl or butyl, Z is -SR<sup>32</sup> and R<sup>32</sup> is



Y is -S-, w = 1, y = 1 and z = 1.

[0054] Examples of diorganotin compounds according to formula (F) include, but are not limited to, the compounds illustrated in Table 5 below.

TABLE 5

$\begin{array}{c} \text{R}^{30}-\text{Sn}-\text{R}^{31} \\    \\ \text{W} \end{array} \quad (\text{F})$			
Diorganotin Compound No.	R <sup>30</sup>	R <sup>31</sup>	W
1	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	S
2	-C <sub>8</sub> H <sub>17</sub>	-C <sub>8</sub> H <sub>17</sub>	O

[0055] Examples of diorganotin compounds according to formula G include, but are not limited to, the compounds in Table 6 below.

TABLE 6

Diorganotin Compound No.	$R^{30}$	$R^{31}$	$Z$ and $Z^1$
C	$\begin{array}{c} \text{O} \\   \\ -\text{CH}_2\text{CH}_2\text{COC}_6\text{H}_5 \end{array}$	Same as $R^{30}$	$\begin{array}{c} \text{O} \\   \\ -\text{SCH}_2\text{CH}_2\text{OCCH}_3 \end{array}$
D	$-\text{CH}_3$	Same as $R^{30}$	$\begin{array}{c} \text{O} \\   \\ -\text{SCH}_2\text{CH}_2\text{OCC}_{17}\text{H}_{35} \end{array}$

[0056] Examples of diorganotin compounds according to formula (H) include, but are not limited to, the compounds in Table 7 below.

TABLE 7

Diorganotin Compound No.	$R^{30}$ and $R^{31}$	$Z$	$Z^1$	$Y$	$n$	$p$	$m$
E	$-\text{CH}_3$	$\begin{array}{c} \text{O} \\   \\ -\text{SCH}_2\text{COC}_{13}\text{H}_{27} \end{array}$	Same as $R^{30}$	$-\text{S}-$	1	1	1
F	$-\text{C}_4\text{H}_9$	$\begin{array}{c} \text{O} \\   \\ -\text{SCH}_2\text{CH}_2\text{OCC}_8\text{H}_{17} \end{array}$	Same as $R^{30}$	$-\text{S}-$	1	1	1

[0057] Examples of diorganotin compounds according to formula (J) include, but are not limited to, the compounds in Table 8 below.

TABLE 8

Diorganotin									
Compound No.	$R^{30}$	$R^{31}$	$Z$	$Y$	$w$	$y$	$z$		
G	$-C_4H_9$	$-C_4H_9$	$  \begin{array}{c}  O \\    \\  -SCH_2CH_2COC_6H_{17}  \end{array}  $	$-S-$	1	1	1		

[0058] The mono-organotin compounds and diorganotin compounds useful in the compositions of this invention may be prepared by methods well-known in the art such as the reaction of a mono- or dialkyltin chloride with a mercaptoalkyl carboxylate or an alkyl thioglycolate in the presence of a base to scavenge hydrogen chloride. Methyltin trichloride, dimethyltin dichloride, butyltin trichloride, dibutyltin dichloride, ethylhexyltin trichloride, and dioctyltin dichloride are examples of organotin halides that are suitable for the preparation of useful stabilizers for this invention. See for example, U.S. Pat. Nos. 3,565,930, 3,869,487, 3,979,359, 4,118,371, 4,134,878 and 4,183,846 all of which are incorporated herein by reference.

[0059] Monosulfides and/or polysulfides of the mercaptoalkyl carboxylates and alkyl thioglycolates are also suitable as metal based stabilizers in the compositions of this invention for improving the resistance of halogen-containing polymers to deterioration when heated to 350°F (177°C) during processing. Polysulfides are mixtures of compounds having from 2 to 10 or more sulfur atoms linked together but compounds having from 2 to 4 sulfur atoms are preferred along with the monosulfides. Said sulfides are made by heating stoichiometric quantities of a mercaptoalkyl ester or alkylthiocarboxylate and an organotin chloride in water and ammonium hydroxide to about 30°C (86°F), slowly adding an alkali metal mono- or polysulfide, and heating the reaction mixture further to about 45°C before separating the product from said mixture. Although stoichiometric quantities are used, the reaction produces several different but related products, some of which have two tin atoms linked together only through sulfide sulfur atoms and have tin atoms linked to hydrocarbonyl groups through carbon atoms and to mercaptoalkyl esters or thioglycolates through mercapto sulfur atoms. Said sulfides contain from about 10 to about 42 % by weight of tin and from about 8 to about 42 % by weight of sulfur.

[0060] Conventional non-metallic stabilizers and antioxidants can also be included in the stabilizer compositions of the present invention to assist in improving the properties of the halogen containing resin. Thus, there can be included 0.01-10%, preferably 0.1-5% based on the resin of sulfur containing compounds such as dilauryl-thiodipropionate, distearyl 3,3'-thiodipropionate, dicyclohexyl-3,3'-thiodipropionate, dioleoyl-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, didecyl-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, diethyl-3,3'-thiodipropionate, lauryl ester of 3-methylmercaptopropionic acid, lauryl ester of 3-butylmercaptopropionic acid, lauryl ester of 3-lauryl mercaptopropionic acid, and phenyl ester of 3-octyl mercaptopropionic acid.

[0061] Phenolic antioxidants can also be added in an amount of 0.01-10%, preferably 0.1-5% of the halogen-containing resin. Examples of such phenols include 2,6-di-t-butyl-p-cresol, butylated hydroxyanisole, propyl gallate, 4,4'-thiobis(6-t-butyl-m-cresol), 4,4'-cyclohexyldenediphenol, 2,5-di-t-amyl hydroquinone, 4,4'-butylidene bis(6-t-butyl-m-cresol), hydroquinone monobenzyl ether, 2,2'-methylene-bis(4-methyl-6-t-butyl phenol), 2,6-butyl-4-decyloxy phenol, 2-t-butyl-4-dodecyloxy phenol, 2-t-butyl-4-dodecyloxy phenol, 2-t-butyl-4-octadecyloxy phenol, 4,4'-methylene-bis(2,6-di-t-butyl phenol), p-amino phenol, N-lauryloxy-p-amino phenol, 4,4'-thiobis(3-methyl-6-t-butyl phenol), bis [o-(1,1,3,3-tetramethyl butyl)phenol] sulfide, 4-acetyl-β-resorcylic acid, A-stage p-t-butylphenolformaldehyde resin, 4-dodecyloxy-2-hydroxybenzophenone, 3-hydroxy-4-(phenylcarbonyl) phenyl palmitate, n-dodecyl ester of 3-hydroxy-4-(phenyl carbonyl) phenoxyacetic acid, and t-butyl phenol.

[0062] The use of epoxy compounds in an amount of 0.01-5% in the polymer compositions is also valuable. Examples

of such epoxy compounds include epoxidized soya bean oil, epoxidized lard oil, epoxidized olive oil, epoxidized linseed oil, epoxidized castor oil, epoxidized peanut oil, epoxidized corn oil, epoxidized tung oil, epoxidized cottonseed oil, epichlorhydrin/bis-phenol A resins, phenoxy-propylene oxide, butoxypropylene oxide, epoxidized neopentylene oleate, glycidyl epoxystearate, epoxidized  $\alpha$ -olefins, epoxidized glycidyl soyate, dicyclopentadiene dioxide, epoxidized butyl toluate, styrene oxide, dipentene dioxide, glycidol, vinyl cyclo-hexene dioxide, glycidyl ether of resorcinol, glycidol ether of hydroquinone, glycidyl ether of 1,5-dihydroxynaphthalene, epox-idized linseed oil fatty acids, allyl glycidyl ether, butyl gly-cidyl ether, cyclohexane oxide, 4-(2,3-epoxypropoxy) aceto-phenone, mesityl oxide epoxide, 2-ethyl-3-propyl glycidamide, glycidyl ethers of glycerine, pentaerythritol and sorbitol, and 3,4-epoxycyclohexane-1, 1-dimethanol bis-9,10-epoxystearate.

[0063] Likewise there can be used organic phosphites in an amount of 0.01 to 10%, preferably 0.1-5% of the halogen containing resins. The organic phosphites contain one or more, up to a total of three, aryl, alkyl, aralkyl and alkaryl groups, in any combination. The term "trialkylaryl" is inclusive of alkyl, aryl, alkaryl and aralkyl phosphites containing any assortment of alkyl, aryl, alkaryl and aralkyl groups. Exemplary are triphenyl phosphite, tricresyl phosphite, tri (dimethylphenyl) phosphite, tributyl phos-phite, trioctyl phosphite, tridodecyl phosphite, octyl diphenyl phosphite, dioctyl phenyl phosphite, tri(octyl-phenyl) phosphite, tri(nonylphenyl) phosphite, tribenzyl phosphite, butyl dicresyl phosphite, octyl di(octyl-phenyl) phosphite, tri(2-ethyl-hexyl) phosphite, tritolyl phosphite, tri(2-cyclohexylphenyl) phosphite, tri-alpha-naphthyl phosphite, tri(phenylphenyl) phosphite, and tri(2-phenylethyl) phosphite.

[0064] Likewise there can be included polyol stabilizers for vinyl chloride resins in an amount of 0.01-10%. Thus there can be included glycerol, sorbitol, pentaerythritol and mannitol.

[0065] Nitrogen containing stabilizers such as dicyandiamide, melamine, urea, formoguanamine, dimethyl hydantoin, guanidine, thiourea, 2-phenylindoles, aminocrotonates, N-substituted maleimides, and the like also can be included in amounts of 0.1-10%. There can even be included conventional lubricants for vinyl chloride resins such as low molecular weight polyethylene, i.e. polyethylene wax, fatty acid amides, e.g. lauramide and stearamide, bisamides, e.g. decamethylene, bis amide, and fatty acid esters, e.g. butyl stearate, glyceryl stearate, linseed oil, palm oil, decyloleate, corn oil, cottonseed oil, hydrogenated cottonseed oil, etc.

[0066] The stabilizer compositions of this invention may be prepared by blending the components thereof in any convenient manner which produces a homogeneous mixture, such as by shaking or stirring in a container. Likewise, the stabilized compositions of this invention can be incorporated in the halogen-containing organic polymer by admixing the stabilizer composition and polymer, such as, for example, in an appropriate mill or mixer or by any other of the well-known methods which provide uniform distribution of the stabilizer throughout the polymer.

[0067] The stabilizer compositions of this invention are employed in an amount sufficient to impart the desired resistance to heat deterioration to halogen-containing organic polymers. It will be readily apparent to one of ordinary skill in the art, that the precise amount of stabilizer composition used will depend upon several factors, including, but not limited to, the particular halogen-containing organic polymer employed, the temperature to which the polymer will be subjected, and the possible presence of other stabilizing compounds. In general, the more severe the conditions to which the halogen-containing organic polymer is sub-jected, and the longer the term required for resisting degradation, the greater will be the amount of stabilizer composition required. Generally, as little as about 0.20 part by weight of the stabilizer composition per hundred parts by weight of halogen-containing organic polymer will be effective. While there is no critical upper limit to the amount of stabilizer composition which can be employed, amounts in excess of about 10 parts by weight of halogen-containing organic polymer do not give an increase in effectiveness commensurate with the additional amount of stabilizer employed.

[0068] The following examples further illustrate the preparation of blocked mercaptans of this invention, the preparation of stabilizer compositions of this invention, and the advantages of said blocked mercaptans and stabilizer compositions.

#### EXAMPLES 1-14

[0069] The starting materials, the procedure for preparing the latent mercaptans and the percent of residual -SH groups in the latent mercaptan are given in TABLE 9. The total color change of PVC compositions containing said latent mercaptans as part of stabilizer compositions in contrast to that of PVC compositions which are otherwise the same but without the latent mercaptan of this invention are given in TABLE 10.

[0070] A standard PVC pipe formulation containing:

INGREDIENT	AMOUNT
PVC (Shintech SE950)	100.00
Calcium carbonate	5.00 phr

# EP 0 742 259 B1

(continued)

INGREDIENT	AMOUNT
Titanium dioxide	1.00 *
Calcium stearate	0.60 *
Oxidized polyethylene	0.15 *
Paraffin wax	1.20 *
Tin mercaptide of a mercaptoalkyl carboxylate	0.25 *

was processed as the Control on a standard two-roll mill at 199° C with chips taken at one-minute intervals. Then the same formulation except for the addition of the indicated amount of latent mercaptan was also processed on the same roll at the same temperature, taking chips at the same intervals. The total color change (dE), relative to a white tile standard, was measured using a Hunter colorimeter. The dE values given in TABLE 10 for the Control are averages of the values measured in the 12 tests which paralleled the tests of the stabilizer compositions of Examples 1-12.

## Examples 15-18

[0071] The standard PVC pipe formulation of Examples 1-14 was used and the heat stabilization afforded by latent mercaptans of FORMULAS 4, 2, and 18 were tested at different levels as shown in Table 11.

TABLE 9

Example No.	FORMULA	Procedure	% SH
1	2	A	0.31
2	3	A	0.10
3*	4	A	0.17
4	10	A	0.10
5	11	B	0.10
6	12	C	0.20
7	13	B	13.2
8	14	A	0.10
9	15	E	0.10
10	16	D	0.35
11	17	D	0.30
12**	18	A	0.25
13	21	A	0.30
14	25	C	0.20

\* Also contains minor amounts of FORMULAS 5-9.

\*\* Also contains minor amount of 19.

TABLE 10

Example		dE at One-minute Intervals									
	phr	1	2	3	4	5	6	7	8	9	10
Control	---	5.6	7.2	8.1	9.4	11.2	13.7	17.0	20.8	23.8	25.7
1	0.10	3.9	4.2	4.6	5.5	8.3	12.1	16.6	20.0	23.6	26.7
2	0.15	4.0	3.9	4.7	5.5	7.0	10.3	14.0	17.6	22.1	26.2
3	0.15	4.0	4.7	4.6	5.2	6.7	8.5	11.3	14.1	18.0	21.3
4	0.28	3.9	5.0	5.5	6.1	7.6	11.7	16.7	20.5	24.2	25.5
5	0.25	5.3	6.2	6.8	7.7	9.3	13.8	18.3	22.1	24.2	25.5
6	0.04	3.0	3.5	4.4	5.8	9.5	13.8	18.3	22.2	23.9	25.6
7	0.12	4.9	5.7	6.5	6.8	7.6	8.9	11.1	14.3	17.1	20.9
8	0.15	6.6	6.7	7.0	7.2	7.8	9.9	12.3	16.3	20.1	23.3
9	0.20	4.3	5.3	6.3	8.5	10.9	14.6	18.6	22.2	24.5	26.8
10	0.30	4.9	5.2	5.6	6.5	7.5	10.6	14.8	18.5	22.0	24.2
11	0.25	6.3	6.6	6.5	7.0	8.2	11.6	16.0	19.4	22.0	23.1
12	0.10	3.5	4.3	5.4	6.4	8.0	10.7	14.1	17.4	21.4	24.7
13	0.10	4.1	4.7	4.7	5.5	6.7	10.0	13.8	17.4	20.1	22.8
14	0.10	4.7	5.6	6.0	6.6	7.3	8.2	16.3	12.9	16.1	18.6



TABLE 11

Example			dE at One-minute Intervals									
	FORMULA	phr	1	2	3	4	5	6	7	8	9	10
Control	---	---	5.6	7.2	8.1	9.4	11.2	13.7	17.0	20.8	23.8	25.7
15	4	0.28	4.2	4.6	4.9	5.9	7.6	10.7	13.0	16.5	20.2	24.6
16	2	0.28	3.8	4.0	4.7	5.3	7.6	10.0	13.2	16.8	21.5	26.3
17	4	0.03	4.4	5.4	5.9	6.4	6.6	7.8	10.0	12.4	14.7	17.1
18	18	0.05	3.5	5.4	5.3	6.2	7.5	8.7	10.2	12.7	10.3	17.8

EP 0 742 259 B1

EXAMPLE 19

[0072] A standard clear PVC formulation containing:

INGREDIENT	AMOUNT
PVC (OCCIDENTAL 190)	100.00
PROCESS AID	1.50 phr
IMPACT MODIFIER	6.00 *
LOXOL G-16	1.00 *
LOXOL G-70	0.70 *
OXIDIZED POLYETHYLENE	0.20 *
EPOXIDIZED SOYBEAN OIL	1.00 *
METHYLTINTHIOGLYCOLATE	1.25 *

was processed as a Control on a standard two-roll mill (30F/40R) at 187°C with chips taken at two-minute intervals. Then the same formulation except for decreased stabilizer level and the addition of the amount of latent mercaptan shown below was also processed on the same roll at the same temperature, taking chips at the same intervals. The total color change (dE) was measured versus a white tile standard using a Hunter colorimeter.

INGREDIENT	AMOUNT (PHR)
METHYLTINTHIOGLYCOLATE	1.00
COMPOUND #4	0.25

TABLE 12

dE at Two Minute Intervals											
	2	4	6	8	10	12	14	16	18	20	22
Control	15.0	15.9	17.1	17.3	18.7	20.1	21.5	23.6	26.8	31.7	38.2
Ex. 19	15.1	14.6	15.1	15.4	15.7	16.9	18.5	20.7	23.7	27.3	34.5

**EXAMPLE 20**

[0073] <sup>1</sup>H-NMR spectroscopy was used to determine the molecular structure of 2-S-(mercaptoethylcapryl)tetrahydrofuran (FORMULA 24) which was prepared by adding 42.0 grams (0.50 mole) of 3,4-dihydropyran to 112.2 grams (0.50 equivalent) of mercaptoethylcaprate (14.7 % SH) over a period of 45 minutes while maintaining a nitrogen atmosphere and a temperature below 35 °C and then heating it to 50°C and holding that temperature for 1.5 hours. After cooling the solution, it was washed with two 200 ml portions of a 10 % sodium bicarbonate solution in water, followed by a 200 ml wash with water. The organic layer was dried with MgSO<sub>4</sub> to yield a light yellow liquid having an SH content of less than 0.5 percent as determined by titration with a 0.100 N iodine solution in isopropanol. The <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ) spectrum was: 2.3 (2H, t, -C(=O)-CH<sub>2</sub>-CH<sub>2</sub>), 2.8 (2H, m, -S-CH<sub>2</sub>-CH<sub>2</sub>-), 4.2 (2H, m, -S-CH<sub>2</sub>CH<sub>2</sub>-O-), 4.9 (1H, m, -O-CH(-S-CH<sub>2</sub>-)-CH<sub>2</sub>-CH<sub>2</sub>-). The total color change (dE) of a PVC composition containing 0.13 phr of the latent mercaptan of this example was measured versus a white tile standard using a Hunter colorimeter at one minute intervals. At one minute, it was 4.2; at five minutes, it was 8.4.

**EXAMPLE 21**

[0074] <sup>1</sup>H-NMR spectroscopy was used to determine the molecular structure of 1-S-(2-hydroxyethylthio)-1-phenylmethane (FORMULA 11) which was prepared by adding 135.0 grams of a 20% methanol solution of sodium methoxide to 39.1 grams (0.50 mole) of 2-mercaptoethanol and 63.3 (0.50 mole) grams of benzyl chloride under nitrogen over a period of 45 minutes while keeping the temperature below 50°C, then heating the solution to 60° C and holding it there for 6 hours. After cooling the solution, it was washed with two 200 ml portions of water, dried with magnesium sulfate, and stripped of solvent at 90°C and 10mm Hg to yield a light yellow liquid having an SH content of less than 0.5 percent as determined by titration with a 0.100N iodine solution in isopropanol. The <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ) spectrum was: 2.6 (2H, t, -S-CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.6 (2H, t, -CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.7 (2H, s, Ar-CH<sub>2</sub>-S-), 7.3 (5H, m, Ar-H); the <sup>13</sup>C-NMR (CDCl<sub>3</sub>, δ) spectrum was 33.9 (-S-CH<sub>2</sub>-), 35.8 (Ar-CH<sub>2</sub>-) and 126.9-138.6 (Ar).

**EXAMPLE 22**

[0075] <sup>1</sup>H-NMR spectroscopy was used to determine the molecular structure of 1-S-(2-hydroxyethylthio)-1-(2-hydroxyphenyl)methane (FORMULA 12) which was prepared by heating a stirred mixture of 31.5 grams (0.40 mole) of 2-mercaptoethanol and 50 grams (0.40 mole) of 2-hydroxy benzyl alcohol in 75 grams of toluene to 40°C under nitrogen and adding 0.21 gram of 70% methanesulfonic acid, heating it to 65° C and holding it there for 45 minutes. After cooling the solution, it was washed with 100 mls of 10% aqueous sodium bicarbonate and 100 mls of water, dried with magnesium sulfate, and stripped of solvent at 50°C and 10 mm Hg to yield a tan viscous oil having an SH content of less than 0.3 percent as determined by titration with a 0.100N iodine solution in isopropanol. The product was purified by column chromatography through silica gel using ethyl acetate/methanol as the elution solvent to obtain a light yellow oil. The <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ) spectrum was: 2.5 (2H, t, -S-CH<sub>2</sub>-CH<sub>2</sub>-), 3.6 (2H, t, -CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.7 (2H, s, Ar-CH<sub>2</sub>-S-), 6.6-7.2 (5H, m, Ar-H); the <sup>13</sup>C-NMR (CDCl<sub>3</sub>, δ) spectrum was 31.1 (-S-CH<sub>2</sub>CH<sub>2</sub>-), 33.5 (Ar-CH<sub>2</sub>-S-), 61.1 (-CH<sub>2</sub>CH<sub>2</sub>-OH and 116.5-154.3 (Ar).

**EXAMPLE 23**

[0076] <sup>1</sup>H-NMR spectroscopy was used to determine the molecular structure of 1-S-(2-hydroxyethylthio)-1-methyl-1-N-pyrrolidinonylmethane (FORMULA 2) which was prepared by adding 55.57 grams (0.50 mole) of 1-vinyl-2 pyrrolidinone with stirring to a solution of 39.06 grams (0.50 mole) of 2-mercaptoethanol and 0.14 gram of 70% methanesulfonic acid while maintaining the temperature below 40°C and an atmosphere of nitrogen in the reaction vessel. The reaction mixture was heated to 60° C and held there for one hour. After cooling the solution, it was diluted with 75 mls of diethyl ether, washed with two 100 ml portions of water and 25 mls of saturated aqueous sodium bicarbonate, dried with magnesium sulfate, and stripped of solvent at 50°C and 10 mm Hg to yield a light yellow oil having an SH content of less than 0.5 percent as determined by titration with a 0.100N iodine solution in isopropanol. The <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ) spectrum was: 1.4 (3H, d, CH<sub>3</sub>-CH), 2.1 (2H, q, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.4 (2H, t, -S-CH<sub>2</sub>-CH<sub>2</sub>-), 2.5 (2H, t, -CH<sub>2</sub>-C(=O)-), 3.4 (2H, t, -CH<sub>2</sub>-CH<sub>2</sub>-N), 3.7 (2H, t, -CH<sub>2</sub>CH<sub>2</sub>-OH), 5.6 (1H, q, N-CH(-CH<sub>3</sub>)-S-); the <sup>13</sup>C-NMR (CDCl<sub>3</sub>, δ) spectrum was 17.7 (CH-CH<sub>3</sub>), 19.2 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 31.3 (CH<sub>2</sub>-CH<sub>2</sub>-C(=O)-), 33.4 (-S-CH<sub>2</sub>CH<sub>2</sub>-), 41.8 (N-CH<sub>2</sub>-CH<sub>2</sub>-), 51.5 (N-CH(-CH<sub>3</sub>)-S-), 61.6 (-S-CH<sub>2</sub>CH<sub>2</sub>-OH), 175.5 (-CH<sub>2</sub>C(=O)-N).

**EXAMPLE 24**

[0077] To 28.4 grams (0.36 mole) of 2-mercaptoethanol under nitrogen, there was added 0.22 gram of p-toluenesul-

# EP 0 742 259 B1

fonic acid, immediately followed by the addition of 60.0 grams (0.36 mole) of cresyl glycidyl ether with stirring over a period of 60 minutes while maintaining the temperature at 50° C. The mixture was then heated to 65° C and held there for 2.5 hours. After cooling, the solution was washed with sodium bicarbonate two-150 ml portions of water containing 25mls of saturated aqueous sodium bicarbonate solution, then dried with magnesium sulfate to yield a clear oil with < 0.4 % SH as determined by titration with 0.100 N iodine solution in isopropanol. The molecular structure of the product, 2-hydroxy-3-(2-hydroxyethylthio)propyl o-methylphenyl ether (FORMULA 16), was determined by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. <sup>1</sup>H-NMR (CD<sub>3</sub>COCD<sub>3</sub>, δ): 2.2 (3H, s, ArCH<sub>3</sub>), 2.8 (4H, m, -CH<sub>2</sub>-S-), 3.7 (2H, m, -CH<sub>2</sub>-OH), 4.1 (2H, dd, Ar-O-CH<sub>2</sub>-), 4.6 (1H, m, -CH(OH)-), 6.8-7.2 (4H, m, Ar-H); <sup>13</sup>C-NMR (CD<sub>3</sub>COCD<sub>3</sub>C, δ): 16.3 (Ar-CH<sub>3</sub>), 36.8 (-S-CH<sub>2</sub>-), 62.3 (-CH<sub>2</sub>-OH), 70.1 (-CH-OH), 70.5 (Ar-O-CH<sub>2</sub>-), 111.9-157.8 (Ar).

## EXAMPLES 25 & 26

[0078] As another aspect of this invention, it has been discovered that antioxidants activate the latent mercaptans to enhance the heat stability of PVC compositions during processing. The PVC pipe formulations of Example 25 (latent mercaptan alone) and Example 26 (latent mercaptan + an antioxidant) are compared with the Control and Comparative Example 1 (CE 1) in TABLE 14. Each was processed on a standard two-roll mill at 199° C. Chips of the PVC formulation were taken at one-minute intervals. The enhanced heat stability of the formulation of Example 26 is evident. As a comparison of the results for the Control and CE 1 shows, the antioxidant does not, by itself, enhance the effect of the alkyltin mercaptide.

INGREDIENT	EXAMPLE			
	Control	25	26	CompEx 1
PVC (Shintech SE950)	100.00	100.00	100.0	100.0
Calcium carbonate	5.00	5.00	5.00	5.00
Titanium dioxide	1.00	1.00	1.00	1.00
Calcium stearate	0.60	0.60	0.60	0.60
Oxidized polyethylene	0.15	0.15	0.15	0.15
Paraffin wax	1.20	1.20	1.20	1.20
Alkyltin mercaptide of a mercaptoalkyl carboxylate	0.25	0.25	0.25	0.25
Latent mercaptan *	0.00	0.15	0.15	0.00
IRGANOX 1010 antioxidant	0.00	0.00	0.20	0.20

\* Isomers of FORMULAS 4-9

TABLE 14

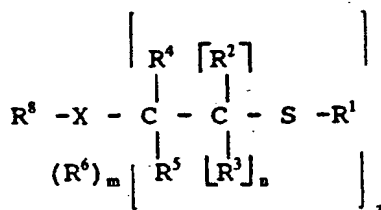
Ex.No.	dE values at One Minute Intervals										
	1	2	3	4	5	6	7	8	9	10	11
Cont.	6.2	7.5	8.3	9.5	11.2	13.2	16.8	20.6	23.7	25.2	27.2
25	4.0	4.8	5.0	5.6	7.1	9.4	12.7	15.6	18.7	22.0	25.2
26	4.3	4.6	5.0	5.2	5.9	7.7	10.2	13.2	15.8	18.8	21.5
CE 1	5.3	7.6	8.3	9.3	11.0	13.1	16.8	20.0	23.2	25.1	26.6

# EP 0 742 259 B1

[0079] As was mentioned above, the latent mercaptans of this invention are also intermediates for the preparation of primary heat stabilizers, anti-oxidants, anti-microbial agents, odor masks, and photostabilizers. Primary heat stabilizers, for example, may be made from latent mercaptans having a phenolic, carboxylate, or a free mercaptan functionality by reaction with a metal or organometal oxide, hydroxide, or halide such as calcium hydroxide, barium hydroxide, methyltin trichloride and dimethyltin dichloride. Phenols, for example, yield compounds having the general formula

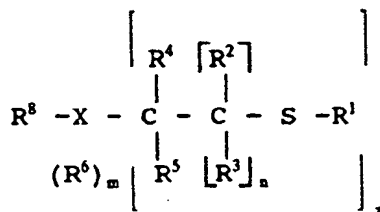


wherein A is Sn, Ba, Ca, Al, monoalkyltin, dialkyltin, trialkyl tin, B is



m and n are 0 or 1, X is aryl, alkaryl, or haloaryl, R<sup>8</sup> is O<sup>-</sup> or S<sup>-</sup>, z is 1 or 2, and b is from 1 to 4.

[0080] As another aspect of this invention then, a compound of the Formula AB<sub>b</sub> wherein A is dibutyltin, B is



m = 0, n = 0, z = 1; X is phenyl, R<sup>4</sup> and R<sup>5</sup> are hydrogen, R<sup>8</sup> is O<sup>-</sup>, R<sup>1</sup> is hydroxyethyl and b is 2, was prepared by the reaction of dibutyltin oxide with 1-S-(2-hydroxyethylthio)-1-(2-hydroxyphenylmethane) (FORMULA 12) as further described in Example 27.

## EXAMPLE 27 and COMPARATIVE EXAMPLE 2

[0081] Twenty grams (0.08 mole) of dibutyltin oxide, 29.61 grams (0.16 mole) of 1-S-(2-hydroxyethylthio)-1-(2-hydroxyphenylmethane), and 150 mls of toluene were heated under a nitrogen atmosphere in a round bottom flask equipped with a Dean-Stark trap. The azeotropic distillation of water was carried out at 108-111°C and the theoretical amount (0.7 ml) was collected after about two hours. The toluene was removed by distillation at 10 mm Hg and a maximum temperature of 110°C. A yellow oil having little or no odor was obtained. The theoretical tin content is 19.7%; the tin content found was 20.2%. A satisfactory product of this invention was thus obtained.

[0082] In TABLE 15, the stabilization of a standard PVC pipe formulation by the product of Example 27 at a level of 0.25 phr is compared with that of dibutyltin diphenate at the same level (Comparative Example 2, made according to the general procedure of Example 27 except that phenol was substituted for the 1-S-(2-hydroxyethylthio)-1-(2-hydroxyphenylmethane). The resulting formulations were processed on a standard two-roll mill at 199°C with chips being taken at one-minute intervals. The standard formulation, as follows, was tested as the Control:

PVC (Shintech SE950)	100.00
Calcium carbonate	5.00
Titanium dioxide	1.00
Calcium stearate	0.60
Oxidized polyethylene	0.15

## EP 0 742 259 B1

(continued)

Paraffin wax	1.20
--------------	------

TABLE 15

Example	dE at One-minute Intervals					
	1	2	3	4	5	6
Control	19.4	33.5	40.3	43.0	40.3	39.3
Comp Ex 2	12.4	22.1	33.0	35.7	35.7	34.1
27	7.9	15.3	21.7	29.5	36.8	41.3

**EXAMPLE 28**

[0083] To a solution containing 22.58 grams (0.106 mole) 1-S-hydroxyethylthiol-1-(2-hydroxyphenyl)propane, 14.47 grams (0.053 mole) 2-mercaptoethyl-(4-methoxybenzyl)thioacetate, 17.94 grams (0.177 mole) triethylamine, and 50 ml of dichloromethane is added dropwise over a period of one hour at 8°C a solution of 15.00 grams (0.053 mole) of butyltintrichloride in 50 ml dichloromethane with stirring under a nitrogen atmosphere. The solution is then slowly warmed to 40°C and held for one hour after which it is cooled to room temperature, transferred to a separatory funnel, and washed twice with 150 ml of water. After drying with magnesium sulfate, the product is stripped of solvent at 50°C under 15 mm pressure to yield an amber oil. The product was analyzed for tin content, 14.5% (14.2% theory), and titratable SH, 4.0% (4.0% theory). A satisfactory product of this invention was thus obtained.

[0084] A standard pipe formulation containing the following components:

INGREDIENT	AMOUNT
PVC (Shintech SE950)	100.00
Calcium carbonate	5.00 phr
Titanium dioxide	1.00 "
Paraffin wax	1.20 "
Calcium stearate	0.60 "
Oxidized Polyethylene	0.15 "

was processed with 0.27 phr of the above protected mercaptan stabilizer and in the absence of stabilizer (CONTROL) on a standard two-roll mill (30F/40R) at 199°C with chips taken at one minute intervals. The total color change (dE) was measured versus a white tile standard using a Hunter colorimeter and is shown in Table 16.



TABLE 16

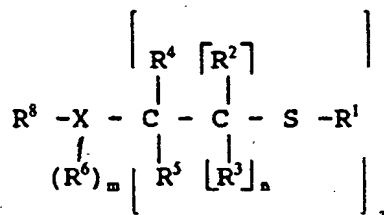
Example	dE at One-minute Intervals									
	1	2	3	4	5	6	7	8	9	10
Control	19.0	30.8	37.4	41.5	41.4	41.8	41.9	38.6	37.6	36.2
28	5.8	8.0	9.7	11.0	12.9	15.2	17.1	19.4	22.3	24.3

[0085] Anti-oxidants also may be made from latent mercaptans having a phenolic hydroxyl group by their reaction with phosphorus trichloride or a phosphite having one, two, or three alkoxy, aryloxy, aralkoxy, alkaryloxy, or haloaryloxy

groups to give a



compound wherein P is phosphorus, Q is an alkoxy, aryloxy, aralkoxy, alkaryloxy, or haloaryloxy radical, p is 1 or 2 and B is



wherein m and n are 0 or 1; z is 1 or 2; R<sup>1</sup> is an alkyl, alkylene, cycloalkyl, cycloalkoxyl, aryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, mercaptoalkoxycarbonylalkyl, hydroxyaryl, mercaptoaryl, carboxyalkyl, carboxyaryl, or acyl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are hydrogen, a hydroxyl, mercapto, alkyl, alkylene, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxy(hydroxyaryl), or mercaptoaryl group having from 1 to 22 carbon atoms; X is aryl, haloaryl or arylcycloalkyl, and R<sup>8</sup> is O<sup>-</sup>.

[0086] Also, the latent mercaptans of this invention wherein the blocking or protecting group includes chemical functionality may provide additional benefit in polymer processing and/or performance. The disagreeable odor generated by primary mercaptan-containing stabilizers during the processing of PVC is masked in latent mercaptans exemplified by the compound of FORMULA 21 and its isomers, and the compound of FORMULA 25. Thus, this invention provides a means for masking the odor of mercaptans while maintaining the function of the mercaptan as a synergist for improved color-hold.

[0087] It also has been found that the latent mercaptans of this invention are useful as the sole heat stabilizer for a flexible PVC formulation. Suitably, the amount of the latent mercaptan for this use may be from about 1 % to about 10 % by weight of the total weight of the stabilized PVC composition. This use of the latent mercaptans of this invention is exemplified in Examples 29 and 30 and by the test results shown in Table 17.

#### EXAMPLES 29 and 30

[0088] A standard flexible PVC formulation containing:

INGREDIENT	AMOUNT
PVC (GEON 30)	100.0
DIOCTYL PHTHALATE	25.0 phr
EPOXIDIZED SOYBEAN OIL	4.0 "
OXIDIZED POLYETHYLENE	0.2 "
STEARIC ACID	0.5 "

was processed using a Brabender Plasticorder at 200°C/80 rpm with chips being taken at two minute intervals. Then the same formulation except for the addition of 5.0 phr of the latent mercaptan of the Formula indicated in Table 17 was also processed at the same intervals. The total color change (dE) was measured versus a white tile standard using a Hunter colorimeter.

#### EXAMPLE 31

[0089] A standard flexible PVC formulation containing:

INGREDIENT	AMOUNT
PVC (GEON 30)	100.00

# EP 0 742 259 B1

(continued)

INGREDIENT	AMOUNT
DIOCTYL PHTHALATE	25.00 phr
EPOXIDIZED SOYBEAN OIL	4.00 "
STEARIC ACID	0.50 "
OXIDIZED POLYETHYLENE	0.20 "
HYDROTALCITE	2.00 "

was processed using a Brabender Plasticorder at 200°C/80 rpm with chips taken at two minute intervals. Then the same formulation except for a decreased part level of hydrotalcite, 1.00 phr, in conjunction with latent mercaptan (CMPD #4), 1.00 phr, was also processed at the same intervals. The total color change (dE), measured versus a white tile standard using a Hunter colorimeter, is shown in Table 18.

TABLE 17

Example	dE at Two-minute Intervals											
	2	4	6	8	10	12	14	16	18	20	22	
Control	49.4	73.3	78.1	80.3	78.3	77.3	77.9	76.2	77.7	83.5	82.7	
29 Formula #4	28.3	41.0	44.6	48.6	48.4	52.0	51.6	50.5	52.0	50.2	51.5	
30 Formula #18	33.0	43.7	47.4	49.3	50.0	51.4	53.1	55.0	60.4	64.5	67.2	

TABLE 18

Ex.	dE at Two-minute Intervals											
	2	4	6	8	10	12	14	16	18	20	22	24
Cont.	30.0	36.3	42.3	48.3	52.3	55.8	66.0	82.9	84.5	CHARRED		
31	28.5	36.0	42.2	44.9	45.2	47.4	58.2	73.5	73.7	70.7	68.7	66.3

## EP 0 742 259 B1

[0090] The use of the latent mercaptans of this invention along with a mixed metal heat stabilizer for flexible PVC formulations is shown in the following example.

### EXAMPLE 32

[0091] A standard flexible PVC formulation containing:

INGREDIENT	AMOUNT
PVC (GEON 30)	100.0
DIOCTYL PHTHALATE	25.0 phr
EPOXIDIZED SOYBEAN OIL	4.0 "
OXIDIZED POLYETHYLENE	0.2 "
STEARIC ACID	0.5 "
Ba/Zn PHENATE	2.5 "

was processed as a Control using a Brabender Plasticorder at 200°C/80 rpm with chips being taken at two minute intervals. Then the same formulation except for the addition of 2.0 phr of the latent mercaptan of Formula 4 was also processed at the same intervals. The total color change (dE) was measured versus a white tile standard using a Hunter colorimeter.

### EXAMPLE 33

[0092] A flexible PVC formulation, similar to that of Example 32 except that the amounts of dioctyl phthalate and epoxidized soy bean oil were 40 and 8.58 phr, respectively, and the phenate was replaced by a mixture of a methyltin carboxylate (0.60 phr) and a zinc carboxylate (0.27 phr) was used as a Control and 0.75 phr of the latent mercaptan of Formula 4 was added to exemplify this invention. Each was processed as in Example 32 except that the Plasticorder was operated at 60 rpm. The color changes of the formulations of Examples 32 and 33 are given in Table 19.

TABLE 19

Example	dE at Two-minute Intervals										
Minutes	2	4	6	8	10	12	14	16	18	20	22
Control (32)	23.1	21.1	20.8	20.9	19.9	20.8	24.7	27.2	33.2	41.2	51.2
32	21.4	21.1	20.9	21.9	22.6	25.8	26.0	31.1	35.0	39.2	42.9
Control (33)	26.1	27.4	27.6	29.2	30.1	31.6	33.6	33.5	38.1	38.8	39.5
33	24.8	24.1	24.3	24.3	23.7	24.7	25.5	24.8	26.7	26.3	28.0

dE at Two-minute Intervals							
Minutes	24	26	28	30	32	34	36
Control	(CHARRED)						
32	43.8	48.5	51.1	52.3	55.5	61.5	74.0 (CHARRED)

EP 0 742 259 B1

[0093] Example 34 below illustrates the use of a hybrid mercaptan of this invention which contains both a blocked mercapto group and a free mercaptan group. The hybrid structures, as in FORMULA 13 above, function as ligands for metallic-based stabilizers and as heat stabilizers by themselves. Table 20 shows the improved early color when the hybrid is used.

EXAMPLE 34 and Comparative Example 3

[0094] A standard PVC pipe formulation containing:

INGREDIENT	AMOUNT
PVC (Shintech SE 950)	100.00
Calcium carbonate	5.00 phr
Titanium dioxide	1.00 "
Paraffin wax	1.20 "
Calcium stearate	0.60 "
Oxidized polyethylene	0.15 "
Tin mercaptide of a mercaptoalkyl carboxylate	0.25 "

was processed as a Control on a dynamic two-roll mill at 199°C (30F/40R) with chips being taken at one minute intervals. Then the same formulation except for the addition of 0.11 phr of 2-mercaptoethylcaprate (Comparative Example 3) or 0.12 phr of the latent mercaptan of FORMULA 13 was processed at the same intervals. The total color change (dE) was measured versus a white tile standard using a Hunter colorimeter.

TABLE 20

Example	dE at One-minute Intervals										
	1	2	3	4	5	6	7	8	9	10	11
Control	5.7	7.6	8.8	9.6	11.4	13.1	16.5	19.7	22.9	25.2	26.6
CE 3	6.0	7.0	7.4	8.1	9.2	10.5	12.7	14.8	18.0	21.7	24.6
<sup>34</sup> Formula #13	4.9	5.7	6.5	6.8	7.6	8.9	11.1	14.3	17.1	20.9	24.3



[0095] Latent mercaptans exemplified by the compounds of FORMULAS 12 and 20 have anti-oxidant properties that may find use in improving polymer processing and polymer performance. A compound of FORMULA 23 acts as a photostabilizer in a polymer to retard discoloration and loss of physical properties caused by ultra-violet radiation.

[0096] The tendency of a free mercaptan to deactivate a biocide in a product containing a heat stabilizer composition as well is negated by the use of a latent mercaptan of this invention in combination with a metal-based stabilizer as the heat stabilizer composition. The latent mercaptan prepared by the reaction of 3,4-dihydropyran and 2-mercaptoethanol (Formula 4), for example, when tested at a level of 0.5 phr in vinyl films containing dibutyltin bis(2-phenylphenate) had no detrimental effect on the anti-microbial activity of OBPA against *staphylococcus aureus* and *klebsiella pneumoniae* bacteria and a fungal mix including *aspergillus niger*, *penicillium pinophyllum*, *chaetomium globosum*, *aureobasidium pullulans*, and *gliocladium virens*.

[0097] A novel, commercially attractive method for making highly active PVC heat stabilizers which often function also as anti-oxidants, UV stabilizers, odor masks, and/or anti-microbial agents has been developed. It is cost-effective and straightforward. The method comprises the reaction of a *para*-substituted phenol with formaldehyde and an alkali metal hydroxide in dilute aqueous solution at a temperature up to about 60°C, preferably a maximum of about 50°C, and still more preferably from about 35° to about 50°C. The condensation is quenched by cooling the reaction mixture below 20°C, the mixture is neutralized, the resultant condensate is isolated without further purification and is further condensed with a mercaptan-containing compound such as is described hereinabove according to Procedure C, also described hereinabove. On an equivalent weight basis, the ratio of the phenol to formaldehyde is from 1:1 to about 1:1.25 and the ratio of the phenol to alkali metal hydroxide is about 1:1 but a 5 to 10 % excess may be used. The total concentration of reactants in the aqueous hydroxymethylation of the phenol is from about 25 to about 50 % by weight. Examples of suitable phenols include bisphenol A, 4,4'-dihydroxydiphenyl sulfone (bisphenol S), *p*-nonylphenol, *p*-tert-butylphenol, 2,4-di-tert-butylphenol, *p*-methoxyphenol, *p*-propylphenol, and *p*-cresol. Typical sources of formaldehyde include aqueous solutions thereof, paraformaldehyde, neat formaldehyde, and cyclic oligomers thereof.

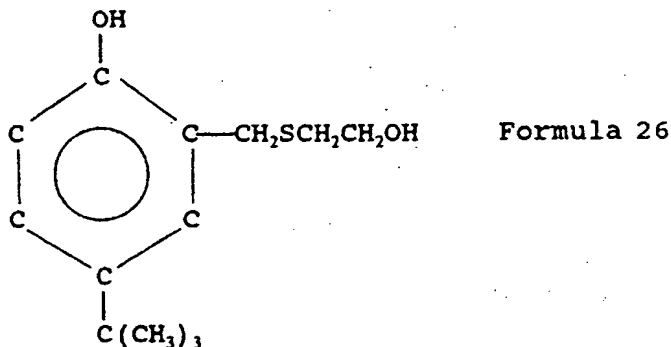
[0098] Examples 35-38 below illustrate the novel method and the activity of the latent mercaptans produced is shown in Tables 21 and 22.

#### EXAMPLE 35

[0099] A nitrogen atmosphere is maintained in a 500 ml 3-neck flask equipped with a condenser and a thermocouple while 20.0 grams (0.122 mole) of 4-allyl-2-methoxyphenol (also known as eugenol) and 100 ml of 5.14 weight/volume % of aqueous sodium hydroxide solution are mixed with stirring while maintaining the temperature of the reaction mixture under 35°C. When the mixture becomes homogeneous, 12.36 grams (0.153 mole) of 37 % aqueous formaldehyde solution is added over a ten minute period at 35°C and then the mixture is slowly heated to 50°C and held there for 3.5 hours, cooled, mixed with 100 ml of ethyl acetate and slowly acidified with dilute hydrochloric acid to a pH of 3 with rapid stirring while maintaining the temperature under 20°C. The organic layer is separated and then combined with a 100 ml ethyl acetate extract of the aqueous layer. The ethyl acetate solution is dried with magnesium sulfate and stripped of solvent at 45°C/15 mm Hg for one hour. Both <sup>1</sup>H and <sup>13</sup>C NMR confirm that the amber liquid residue conforms to the desired intermediate, 4-allyl-2-hydroxymethyl-6-methoxymethyl phenol. Then, a nitrogen atmosphere is established in a 3-neck, 250 ml flask equipped with a condenser and a thermocouple and maintained while 20.0 grams (0.103 mole) of the intermediate and 8.05 grams (0.103 mole) of 2-mercaptoethanol, and 100 ml of toluene, are stirred until homogeneous. The solution is heated to 40°C, 0.06 gram of methanesulfonic acid is added, and the solution is further heated to 65-70°C for 3 hours. The solution is cooled to 25 °C, transferred to a separatory funnel and washed with a saturated sodium bicarbonate solution to neutrality, dried with magnesium sulfate, and stripped at 40°C/5 mm Hg for one hour. The residue is an amber liquid of pleasant odor with 0.1 % residual -SH content, as determined by 0.100 N iodine titration in isopropanol. Both <sup>1</sup>H and <sup>13</sup>C NMR confirm that the residue is 4-allyl-2-methoxy-6-(2-hydroxyethyl-1S-thio)phenol as the major product and unreacted intermediate as the remainder.

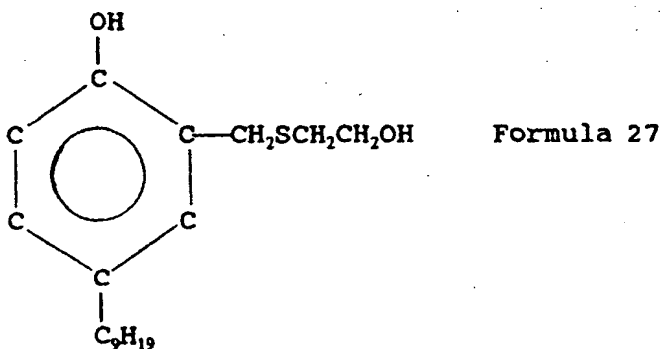
#### EXAMPLE 36

[0100] The general procedure of Example 35 was repeated except that 50 grams (0.333 mole) of *p*-tert-butyl phenol was used, along with 14 grams (0.35 mole) of 98 % sodium hydroxide and 33.73 grams (0.416 mole) of the formaldehyde solution to obtain the intermediate 2-hydroxymethyl-4-tert-butyl phenol. The desired product, 2-(2-hydroxyethyl)thiomethyl-4-tert-butyl phenol, was obtained from 17.2 grams (0.095 mole) of the intermediate and 7.4 grams of the 2-mercaptoethanol (0.095 mole) in 50 ml of toluene, along with 0.10 gram of the catalyst. Structural formula 26 for the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR.

**EXAMPLE 37**

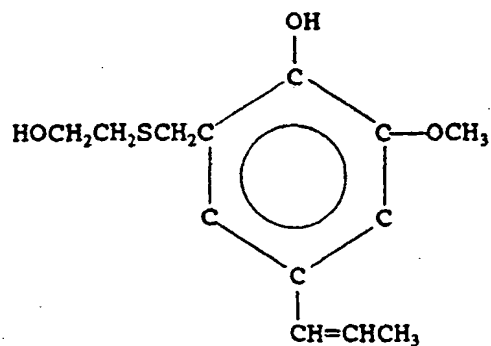
20 [0101] The general procedure of Example 35 was repeated except that 50 grams of *p*-nonyl phenol (0.227 mole) was used, along with 9.73 grams (0.238 mole) of 98 % sodium hydroxide and 23.0 grams (0.284 mole) of the formaldehyde solution to obtain the intermediate 2-hydroxymethyl-4-nonyl phenol. The desired product, 2-(2-hydroxyethyl)thiomethyl-4-nonyl phenol, was obtained from 23.85 grams (0.095 mole) of the intermediate and 7.4 grams of the 2-mercaptoethanol (0.095 mole) in 50 ml of toluene, along with 0.10 gram of the catalyst. Structural formula 27 for the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR.

25

**EXAMPLE 38**

45 [0102] The general procedure of Example 35 was repeated except that 50 grams of 2-methoxy-4-allyl phenol (0.305 mole) was used, along with 13.1 grams (0.32 mole) of 98 % sodium hydroxide and 30.9 grams (0.381 mole) of the formaldehyde solution to obtain the intermediate 2-methoxy-4-allyl-6-hydroxymethyl phenol. The desired product, 2-methoxy-4-allyl-6-(2-hydroxyethyl)thiomethylphenol, was obtained from 18.53 grams (0.095 mole) of the intermediate and 7.4 grams of the 2-mercaptoethanol (0.095 mole) in 50 ml of toluene, along with 0.10 gram of the catalyst. Structural formula 28 for the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR.

50



Formula 28

**EXAMPLE 39**

[0103] A standard PVC pipe formulation containing:

INGREDIENT	AMOUNT
PVC (Shintech SE 950)	100.00
Calcium carbonate	5.00 phr
Titanium dioxide	1.00 "
Paraffin wax	1.20 "
Calcium stearate	0.60 "
Oxidized polyethylene	0.15 "
Dimethyltin mercaptide (ADVASTAB® TM-599T)	0.25 "

was processed as a Control on a dynamic two-roll mill at 187°C (30F/40R) with chips being taken at one minute intervals. The formulation of this invention made by the addition of 0.05 phr of the product of Example 38 had a mild, yet decidedly pleasant odor during processing on the two-roll mill under the same conditions. The total color change (dE) and the Whiteness Index of each are shown in Table 21.

Table 21

Example	dE at one minute intervals									
	1	2	3	4	5	6	7	8	9	10
Control	4.6	6.3	7.0	7.5	8.1	9.4	10.7	12.1	14.4	16.8
41	3.9	4.6	4.8	5.1	5.7	6.7	8.5	10.8	13.7	16.5
Whiteness Index at one minute intervals										
Control	61.2	49.8	45.6	43.0	39.1	31.9	24.9	17.1	6.8	-6.5
41	63.6	58.0	57.3	54.5	50.5	45.1	35.5	24.1	8.8	-5.2

## EP 0 742 259 B1

### EXAMPLE 40

[0104] The standard PVC pipe formulation of Example 39 was again used as a Control and was processed on a dynamic two-roll mill at 187°C (30F/40R) with chips being taken at one minute intervals. The a formulation of this invention made by the addition of 0.03 phr of the product of Example 36 was processed under the same conditions. The total color change (dE) and the Whiteness Index of each are shown in Table 22.

10

15

20

25

30

35

40

45

50

55

Table 22

Example	dE at one minute intervals									
	1	2	3	4	5	6	7	8	9	10
Control	4.4	6.1	6.6	7.4	7.9	8.7	10.1	11.6	13.1	15.9
40	3.6	4.4	4.3	4.8	5.3	6.5	8.0	10.6	13.3	15.5
	Whiteness Index at one minute intervals									
	1	2	3	4	5	6	7	8	9	10
Control	59.8	51.7	47.9	43.2	40.2	35.8	27.5	19.6	11.7	-2.1
40	62.8	60.9	59.7	58.9	53.8	46.7	38.9	25.1	10.9	-0.3

## EP 0 742 259 B1

### EXAMPLE 41 and Comparative Example 4

[0105] The standard PVC pipe formulation of Example 39 was again used as a Control. The formulation of this invention made by the addition of 0.05 phr of the product of Example 37. For comparison, a formulation was made by the addition of 0.05 phr of nonylphenol to the Control. Each was processed on a dynamic two-roll mill at 187°C (30F/40R) with chips being taken at one minute intervals. The total color change (dE) and the Whiteness Index of each are shown in Table 23.

10

15

20

25

30

35

40

45

50

55

Table 23

Example	dE at one minute intervals									
	1	2	3	4	5	6	7	8	9	10
Control	4.7	6.8	7.5	8.0	8.9	9.8	11.4	12.5	14.6	17.0
41	3.7	4.6	4.9	5.3	6.1	7.5	9.1	11.1	14.0	16.4
Comp Ex 4	4.7	6.6	7.2	7.5	8.1	9.1	9.9	11.5	13.7	15.9
	Whiteness Index at one minute intervals									
	1	2	3	4	5	6	7	8	9	10
Control	57.7	46.6	42.5	41.0	35.4	30.1	20.8	15.5	4.0	-7.6
41	63.5	60.4	56.4	55.9	50.0	41.9	33.5	23.3	7.5	-5.1
Comp Ex 4	59.4	48.0	44.8	43.2	39.2	33.8	29.8	20.9	9.2	-2.1



# EP 0 742 259 B1

## EXAMPLES 42-46

[0106] A standard flexible PVC formulation containing:

INGREDIENT	AMOUNT
Geon 30 PVC resin	100.00
Diethyl phthalate	40.00
Epoxidized soybean oil	8.58
Oxidized polyethylene	0.20
Stearic acid	0.50

was processed as the control on a standard two-roll mill at 199°C with chips taken at two minute intervals. Then the same formulation except for the addition of the indicated amount of protected mercaptan and N-substituted maleimides was also processed on the same two-roll mill under the same conditions. The total color change, dE, relative to a white tile standard, was measured using a Hunter colorimeter.

EXAMPLE	INGREDIENT	AMOUNT
CONTROL	NONE	-----
42	Mixture of Formulas 4-9	2.50 phr
43	N-ethylmaleimide	2.50 phr
44	Mixture of Formulas 4-9	1.25 phr
	N-ethylmaleimide	1.25 phr
45	N-phenylmaleimide	2.50 phr
46	Mixture of Formulas 4-9	1.25 phr
	N-phenylmaleimide	1.25 phr

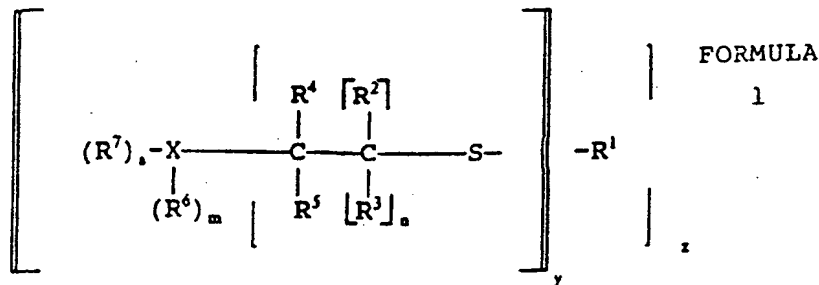
Table 24

Example	dE at two minute intervals									
	2	4	6	8	10	12	14	16	18	20
Control	40.4	55.6	67.9	74.2	75.8	78.5	--	--	--	--
42	25.9	35.0	44.1	45.9	47.8	49.2	49.8	50.6	51.1	52.1
43	28.6	41.2	52.9	58.9	59.6	63.5	--	--	--	--
44	26.8	32.9	40.1	40.7	43.1	43.7	45.7	45.9	46.9	48.3
45	33.8	43.0	53.4	59.4	62.4	61.5	--	--	--	--
46	29.5	34.3	38.5	41.6	44.3	42.5	42.8	43.5	44.5	44.8

[0107] Articles of manufacture contemplated by this invention, e.g. pipe, film, and window profile, are formed from the stabilized compositions of this invention by any of the well-known conventional techniques for forming polymers into shaped articles.

# Claims

1. A composition comprising a halogen-containing polymer and degradation products of a blocked mercaptan present during processing of the composition at an elevated temperature, said products including a free mercaptan and said blocked mercaptan having the structure:

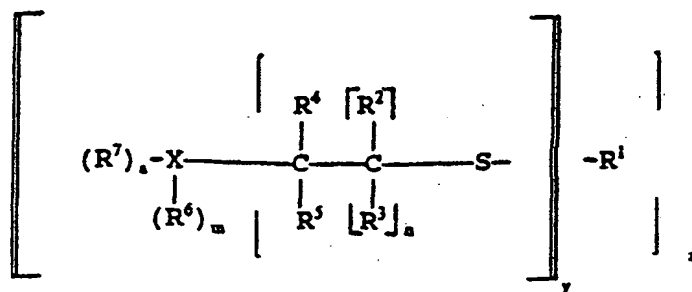


wherein a is 0 or 1, m and n are 0 or 1; y = 1 to 4, z is 1 to 4 when y = 1 and z is 1 when y is more than 1; R<sup>1</sup> is a tetrahydropyranyloxyethyl group or a hydroxyalkyl, acyloxyalkyl, carboxyaryl, or carboxyaryl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> may each independently represent hydrogen, a hydroxyl or mercapto group or an alkyl, alkylene, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxyhydroxyaryl, mercaptoaryl or acyl group having from 1 to 22 carbon atoms X is aryl, haloaryl, alkaryl, aralkaryl, alkoxyaryl, arylcycloalkyl, or a heteroatom, with the proviso that when a is 1 and m is 0, one of the R<sup>1</sup>, R<sup>3</sup>, or R<sup>5</sup> groups may join with R<sup>7</sup> and X to form a heterocyclic moiety with X as a heteroatom of oxygen or sulfur, and when a is 1 and m is 1, R<sup>6</sup> and R<sup>7</sup> may form a heterocyclic moiety in conjunction with X as a nitrogen atom, with the further proviso that when x is aralkaryl, R<sup>6</sup> and R<sup>7</sup> are hydroxyl, a is 1 and m is 1, then z is 1 or 2, and with the still further proviso that when R<sup>6</sup> ≠ hydroxyl or mercapto, z is 1.

2. A composition according to claim 1 wherein R<sup>1</sup> is acyloxyalkyl.
3. A composition according to claim 1 wherein R<sup>1</sup> is hydroxyalkyl.
4. A composition according to claim 3 wherein R<sup>1</sup> is hydroxyethyl.
5. A composition according to claim 3 or claim 4 wherein X is nitrogen, m is 1, R<sup>6</sup> is acyl, R<sup>1</sup> is alkyl and n is 0.
6. A composition according to any one of claims 1 to 4 wherein X is nitrogen, m is 1, R<sup>6</sup> and R<sup>7</sup> form a heterocyclic moiety in conjunction with X, and n is 0.
7. A composition according to any one of claims 1 to 6 wherein X is oxygen, m is 0, R<sup>6</sup> and R<sup>7</sup> form a heterocyclic moiety in conjunction with X, and n is 0.
8. A composition according to any one of claims 1 to 6 wherein X is oxygen, m is 0, R<sup>6</sup> and R<sup>7</sup> form a heterocyclic moiety in conjunction with X, and n is 1.
9. A composition according to any one of claims 1 to 6 wherein X is oxygen, R<sup>7</sup> is phenyl, m is 0, and n is 1.
10. A composition according to any one of claims 1 to 6 wherein X is oxygen, m is 0, n is 1, R<sup>5</sup> is aryloxyalkyl, and R<sup>7</sup> is hydrogen.
11. A composition according to any one of claims 1 to 6 wherein X is oxygen, m is 0, n is 1, R<sup>5</sup> is alkoxyalkyl, and and

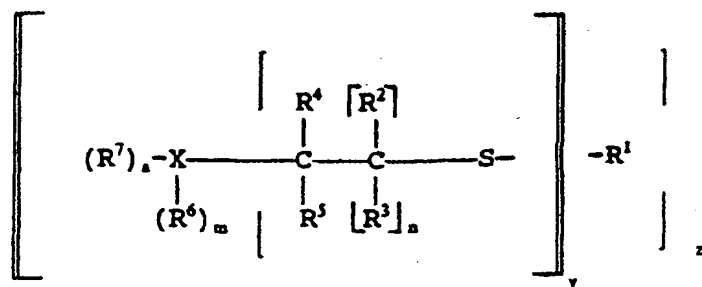
R<sup>7</sup> is hydrogen.

12. A composition according to any one of claims 1 to 4 wherein X is oxygen, m is 0, R<sup>7</sup> and R<sup>1</sup> are methylene groups which join together to form a heterocyclic moiety with X and the sulfur atom, and n is 0.
13. A composition according to any one of claims 1 to 4 wherein X is phenyl, m and n are 0.
14. A composition according to claim 13 wherein R<sup>7</sup> is hydroxyl.
15. A composition according to any one of claims 1 to 4 wherein X is phenyl, R<sup>7</sup> is hydroxyl, m is 0 and n is 1.
16. A composition according to any one of claims 1 to 4 wherein X is phenoxy, m is 0, and n is 1.
17. A composition according to any one of claims 1 to 4 wherein X is benzyl, R<sup>7</sup> is hydroxyl, and m and n are 0.
18. A composition according to any one of claims 1 to 4 wherein X is alkoxyphenyl, R<sup>7</sup> is hydroxyl and m is 0.
19. A composition according to any preceding claim wherein R<sup>3</sup> is alkyl.
20. A composition according to any preceding claim which also includes a biocide.
21. A composition according to claim 20 wherein the biocide is 10,10'-oxybisphenoxyarsine (OBPA).
22. A composition according to any preceding claim wherein the halogen-containing polymer is a vinyl chloride polymer.
23. A composition according to any preceding claim characterized further by the presence of a metallic-based heat stabilizer.
24. A composition according to claim 23 wherein at least one of the metallic-based heat stabilisers is selected from antimony-, barium-, boron, and calcium-, tin-, and zinc-based stabilizers.
25. A composition according to claim 23 or claim 24 wherein the metallic-based heat stabilizer is an organometal compound.
26. A composition according to claim 25 wherein the metallic-based heat stabilizer is an organotin compound.
27. A composition according to claim 26 wherein the organotin compound is an organotin mercaptide.
28. A composition according to claim 27 wherein the mercaptide moiety is an alkyl thioglycolate.
29. A composition according to claim 27 wherein the mercaptide moiety is a mercaptoalkyl carboxylate.
30. A composition according to claim 25 or claim 26 wherein the metallic-based heat stabilizer is an organometal mercaptoester sulfide.
31. A composition according to claim 30 wherein the mercaptide moiety of the organometal mercaptoester sulfide is an alkyl thioglycolate.
32. A composition according to claim 30 wherein the mercaptide moiety of the organometal mercaptoester sulfide is a mercaptoalkyl carboxylate.
33. A polymeric composition comprising a blocked mercaptan having the structure:



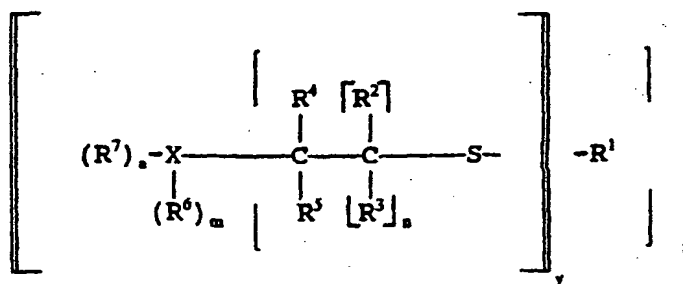
wherein a is 0 or 1, m and n are 0 or 1; y = 1 to 4; z is 1 to 4 when y = 1 and z is 1 when y is more than 1; R<sup>1</sup> is a tetrahydropyranyloxyethyl group or a hydroxyalkyl, acyloxyalkyl, carboxyalkyl or carboxyaryl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently hydrogen, a hydroxyl or mercapto group or an alkyl, alkylenyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxyhydroxyaryl, mercaptoaryl or acyl group having from 1 to 22 carbon atoms; X is arylcycloalkyl or a heteroatom when a = 1 and when a = 0 X is aryl, haloaryl, alkaryl, alkoxyaryl, arylcycloalkyl, or a heteroatom, with the proviso that when a is 1 and m is 0, one of the R<sup>1</sup>, R<sup>3</sup>, or R<sup>5</sup> groups may join with R<sup>7</sup> and X to form a heterocyclic moiety with X as a heteroatom of oxygen or sulfur, and when a is 1 and m is 1, R<sup>6</sup> and R<sup>7</sup> may form a heterocyclic moiety in conjunction with X as a nitrogen atom.

34. A blocked mercaptan having the structure:



wherein a is 0 or 1, m and n are 0 or 1; y = 1 to 4; z is 1 to 4 when y = 1 and z is 1 when y is more than 1; R<sup>1</sup> is a tetrahydropyranyloxyethyl group or a hydroxyalkyl, carboxyalkyl, carboxyaryl, or acyloxyalkyl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently hydrogen, a hydroxyl or mercapto group or an alkyl, alkylenyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxyhydroxyaryl, mercaptoaryl or acyl group having from 1 to 22 carbon atoms; and X is a heteroatom of oxygen, nitrogen or sulfur, with the proviso that when a is 1 and m is 0, one of the R<sup>1</sup>, R<sup>3</sup> or R<sup>5</sup> groups may join with R<sup>7</sup> and X to form a heterocyclic moiety with X as a heteroatom of oxygen or sulfur, and when a = 1 and m is 1, R<sup>6</sup> and R<sup>7</sup> may form a heterocyclic moiety in conjunction with X as a nitrogen atom.

35. A composition for stabilizing PVC consisting essentially of a metallic-based stabilizer for PVC and a latent mercaptan having the formula:

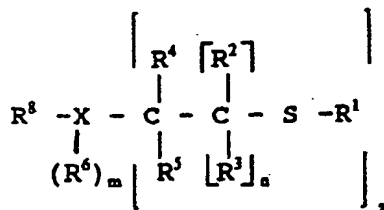


wherein a is 0 or 1, m and n are 0 or 1; y = 1 to 4, z = 1 to 4 when y = 1 and z is 1 when y is more than 1; R<sup>1</sup> is a tetrahydropyranyloxyethyl group or a hydroxyalkyl, carboxyalkyl, carboxyaryl, or acyloxyalkyl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently hydrogen, a hydroxyl or mercapto group or an alkyl, alkylenyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxyhydroxyaryl, mercaptoaryl or acyl group having from 1 to 22 carbon atoms; X is aryl, haloaryl, alkaryl, aralkaryl, alkoxyaryl, arylcycloalkyl, or a heteroatom, with the proviso that when a is 1, one of the R<sup>1</sup>, R<sup>3</sup>, or R<sup>5</sup> groups may join with R<sup>7</sup> and X to form a heterocyclic moiety with X as a heteroatom of oxygen or sulfur, and when m is 1, R<sup>6</sup> and R<sup>7</sup> may form a heterocyclic moiety in conjunction with X as a nitrogen atom, with the further proviso that when x is aralkaryl, R<sup>6</sup> and R<sup>7</sup> are hydroxyl, a is 1 and m is 1, then z is 1 or 2, and with the still further proviso that when R<sup>6</sup> ≠ hydroxyl or mercapto, z is 1.

36. A composition capable of stabilizing a halogen-containing polymer against deterioration caused by heat, said composition comprising one heat stabilizer, said heat stabilizer being the blocked mercaptan of claim 34.
37. A method for the preparation of a heat stabilizer for halogen-containing polymers, said method comprising condensing a *para*-substituted phenol with formaldehyde in the presence of an alkali metal hydroxide in aqueous solution at a temperature of up to 60°C, wherein the ratio of the phenol to formaldehyde is from 1:1 to 1:1.05 on an equivalent weight basis, and the molar ratio of the phenol to alkali metal hydroxide is about 1:1, quenching the condensation by cooling the reaction mixture below 20°C, neutralizing the mixture, isolating the resultant condensate, and further condensing the resultant condensate without further purification with a mercaptan-containing compound selected from alkyl mercaptans, mercapto esters, mercapto alcohols, and mercapto acids at from 40°C to 120°C in the presence of an acid catalyst.
38. A method according to claim 35 wherein the maximum temperature during the phenol/formaldehyde condensation is 50°C.
39. A method according to claim 35 wherein the temperature during the phenol/formaldehyde condensation is from 35°C to 50°C.
40. A method according to claims 35 to 37 wherein the total concentration of phenolic and formaldehyde reactants is from 25 to 50% by weight.
41. A compound having the general formula:



wherein A is Sn, Ba, Ca, Al, monoalkyltin, dialkyltin, trialkyltin, b is from 1 to 4 and B has the general formula:



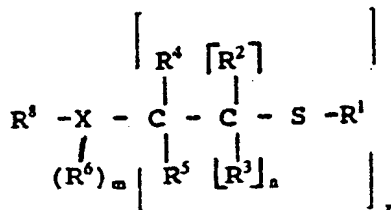
wherein m and n are 0 or 1, X is aryl, alkaryl or haloaryl, R<sup>8</sup> is O<sup>-</sup> or S<sup>-</sup>, z is 1 or 2 and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are as defined in relation to Formula 1 in claim 1.

42. A compound according to claim 41 wherein A is dibutyltin, m = 1, n = 0, z = 1, X is phenyl, R<sup>4</sup> and R<sup>5</sup> are hydrogen, R<sup>8</sup> is O<sup>-</sup>, R<sup>1</sup> is hydroxyethyl and b is 2.

43. A compound having the general formula:

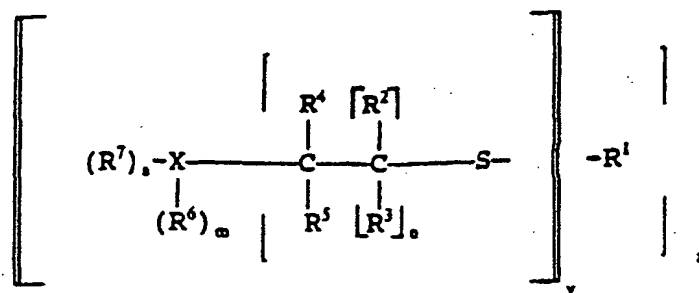


wherein P is phosphorus, Q is an alkoxy, aryloxy, aralkoxy, alkaryloxy or haloaryloxy radical, p is 1 or 2 and B has the general formula:



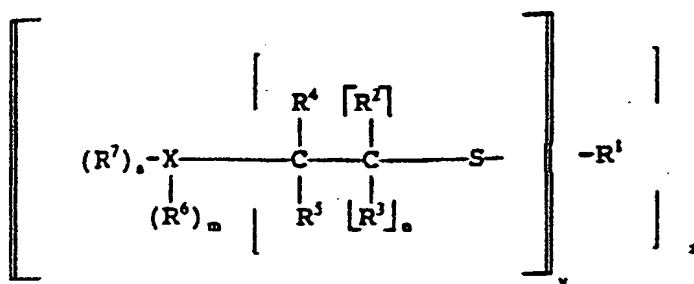
wherein m and n are 0 or 1; z is 1 or 2; R<sup>1</sup> is an alkyl, alkylene, cycloalkyl, cycloalkoxyl, aryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, mercaptoalkoxycarbonylalkyl, hydroxyaryl, mercaptoaryl, carboxyalkyl, carboxyaryl, or acyl group having from 1 to 22 carbon atoms; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are hydrogen, a hydroxyl, mercapto, alkyl, alkylene, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, mercaptoalkyl, hydroxyaryl, alkoxy(hydroxyaryl), or mercaptoaryl group having from 1 to 22 carbon atoms; X is aryl, haloaryl or arylcycloalkyl, and R<sup>8</sup> is O<sup>-</sup>.

44. A polymeric composition comprising a polymer normally susceptible to heat-induced deterioration through autoxidation and an anti-oxidant which is a blocked mercaptan having the structure:



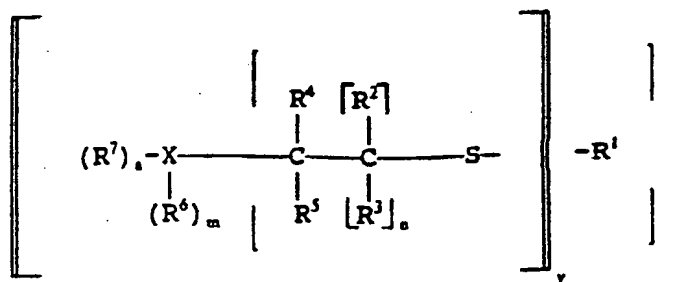
wherein a is 1, m and n are 0, y and z are 1, X is phenyl,  $R^4$  and  $R^5$  are hydrogen,  $R^7$  is o-hydroxy, and  $R^1$  is hydroxyethyl.

45. A polymeric composition comprising a polymer normally susceptible to heat-induced deterioration through autoxidation and an antioxidant which is a blocked mercaptan having the structure:



wherein a is 1, m and n are 0, y is 1, z is 2, X is phenyl,  $R^4$  is hydrogen,  $R^5$  is ethyl,  $R^7$  is o-hydroxy and  $R^1$  is hydroxyethyl.

46. A polymeric composition comprising a halogen-containing polymer, a primary mercaptan-containing heat stabilizer, and odor-masking latent mercaptan having the structure:

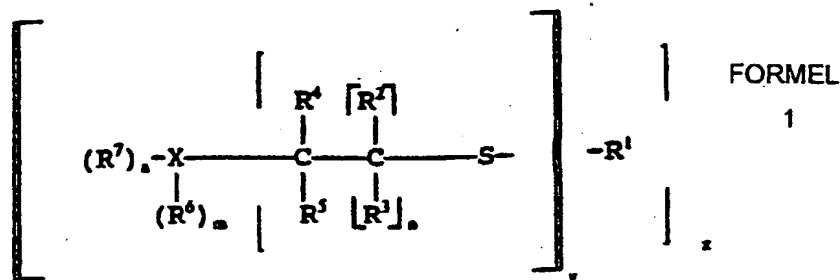


wherein a is 1, m and n are 0, y is 1, z is 1,  $R^1$  is hydroxyalkyl,  $R^4$  is hydrogen,  $R^5$  is hydrogen or alkyl,  $R^7$  is p-hydroxy and X is m-methoxyphenyl.



## Patentansprüche

1. Zusammensetzung mit einem halogenhaltigen Polymer und Abbauprodukten eines blockierten Mercaptans, das während der Verarbeitung der Zusammensetzung bei einer erhöhten Temperatur vorliegt, wobei diese Produkte ein freies Mercaptan und das blockierte Mercaptan mit der Struktur



einschließen, worin a 0 oder 1 ist, m und n 0 oder 1 sind, y 1 bis 4 ist, z 1 bis 4 ist, wenn y 1 ist, und z 1 ist, wenn y mehr als 1 ist, R<sup>1</sup> eine Tetrahydropyranyloxyethylgruppe oder eine Hydroxyalkyl-, Alkoxyalkyl-, Carboxyalkyl- oder Carboxyarylgruppe mit 1 bis 22 Kohlenstoffatomen ist, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> und R<sup>7</sup> jeweils unabhängig voneinander Wasserstoff, eine Hydroxyl- oder Mercaptogruppe oder eine Alkyl-, Alkylenyl-, Aryl-, Halogenaryl-, Alkaryl-, Aralkyl-, Hydroxyalkyl-, Mercaptoalkyl-, Hydroxyaryl-, Alkoxyhydroxyaryl-, Mercaptoaryl- oder Acylgruppe mit 1 bis 22 Kohlenstoffatomen sein können, X Aryl, Halogenaryl, Alkaryl, Aralkaryl, Alkoxyaryl, Arylcycloalkyl oder ein Heteroatom ist, wobei, wenn a 1 und m 0 ist, eine der Gruppen R<sup>1</sup>, R<sup>3</sup> oder R<sup>5</sup> mit R<sup>7</sup> und X unter Bildung eines heterozyklischen Restes mit X als ein Heteroatom Sauerstoff oder Schwefel sein kann, und wenn a 1 ist und m 1 ist, R<sup>6</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X als ein Stickstoffatom bilden können, wobei weiterhin, wenn x Aralkaryl ist, R<sup>6</sup> und R<sup>7</sup> Hydroxyl sind, a 1 ist und m 1 ist, z 1 oder 2 ist, und wobei schließlich, wenn R<sup>6</sup> Hydroxyl oder Mercapto ist, z 1 ist.

2. Zusammensetzung nach Anspruch 1, worin R<sup>1</sup> Acyloxyalkyl ist.
3. Zusammensetzung nach Anspruch 1, worin R<sup>1</sup> Hydroxyalkyl ist.
4. Zusammensetzung nach Anspruch 3, worin R<sup>1</sup> Hydroxyethyl ist.
5. Zusammensetzung nach Anspruch 3 oder Anspruch 4, worin X Stickstoff ist, m 1 ist, R<sup>6</sup> Acyl ist, R<sup>1</sup> Alkyl ist und n 0 ist.
6. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Stickstoff ist, m 1 ist, R<sup>6</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X bilden und n 0 ist.
7. Zusammensetzung nach einem der Ansprüche 1 bis 6, worin X Sauerstoff ist, m 0 ist, R<sup>5</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X bilden und n 0 ist.
8. Zusammensetzung nach einem der Ansprüche 1 bis 6, worin X Sauerstoff ist, m 0 ist, R<sup>5</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X bilden und n 1 ist.
9. Zusammensetzung nach einem der Ansprüche 1 bis 6, worin X Sauerstoff ist, R<sup>7</sup> Phenyl ist, m 0 ist und n 1 ist.
10. Zusammensetzung nach einem der Ansprüche 1 bis 6, worin X Sauerstoff ist, m 0 ist, n 1 ist, R<sup>5</sup> Aryloxyalkyl ist und R<sup>7</sup> Wasserstoff ist.
11. Zusammensetzung nach einem der Ansprüche 1 bis 6, worin X Sauerstoff ist, m 0 ist, n 1 ist, R<sup>5</sup> Alkoxyalkyl ist und R<sup>7</sup> Wasserstoff ist.
12. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Sauerstoff ist, m 0 ist, R<sup>7</sup> und R<sup>1</sup> Ethylengruppen

**EP 0 742 259 B1**

sind, die miteinander unter Bildung eines heterozyklischen Restes mit X und dem Schwefelatom verbunden sind, und n 0 ist.

5 13. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Phenyl ist, m und n 0 sind.

14. Zusammensetzung nach Anspruch 13, worin R<sup>7</sup> Hydroxyl ist.

15. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Phenyl ist, R<sup>7</sup> Hydroxyl ist, m 0 ist und n 1 ist.

10 16. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Phenoxy ist, m 0 ist und n 1 ist.

17. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Benzyl ist, R<sup>7</sup> Hydroxyl ist und m und n 0 sind.

18. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin X Alkoxyphenyl ist, R<sup>7</sup> Hydroxyl ist und m 0 ist.

15 19. Zusammensetzung nach einem der vorausgehenden Ansprüche, worin R<sup>3</sup> Alkyl ist.

20. Zusammensetzung nach einem der vorausgehenden Ansprüche, welche auch ein Biozid einschließt.

20 21. Zusammensetzung nach Anspruch 20, worin das Biozid 10,10'-Oxybisphenoxyarsin (OBPA) ist.

22. Zusammensetzung nach einem der vorausgehenden Ansprüche, worin das halogenhaltige Polymer ein Vinylchloridpolymer ist.

25 23. Zusammensetzung nach einem der vorausgehenden Ansprüche, weiterhin gekennzeichnet durch das Vorhandensein eines Wärmestabilisators auf metallischer Basis.

24. Zusammensetzung nach Anspruch 23, worin wenigstens einer der Wärmestabilisatoren auf metallischer Basis unter Stabilisatoren auf Antimon-, Barium-, Bor- und Calcium-, Zinn- und Zinkbasis ausgewählt ist.

30 25. Zusammensetzung nach Anspruch 23 oder Anspruch 24, worin der Wärmestabilisator auf metallischer Basis eine metallorganische Verbindung ist.

35 26. Zusammensetzung nach Anspruch 25, worin der Wärmestabilisator auf metallischer Basis eine zinnorganische Verbindung ist.

27. Zusammensetzung nach Anspruch 26, worin die zinnorganische Verbindung ein zinnorganisches Mercaptid ist.

40 28. Zusammensetzung nach Anspruch 27, worin der Mercaptidrest ein Alkylthioglycolat ist.

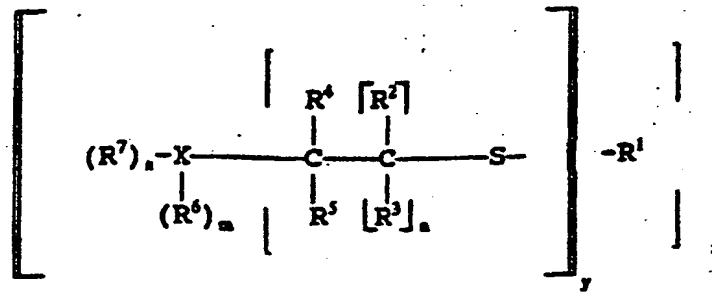
29. Zusammensetzung nach Anspruch 27, worin der Mercaptidrest ein Mercaptoalkylcarboxylat ist.

45 30. Zusammensetzung nach Anspruch 25 oder Anspruch 26, worin der Wärmestabilisator auf metallischer Basis ein metallorganisches Mercaptoestersulfid ist.

31. Zusammensetzung nach Anspruch 30, worin der Mercaptidrest des metallorganischen Mercaptoestersulfids ein Alkylthioglycolat ist.

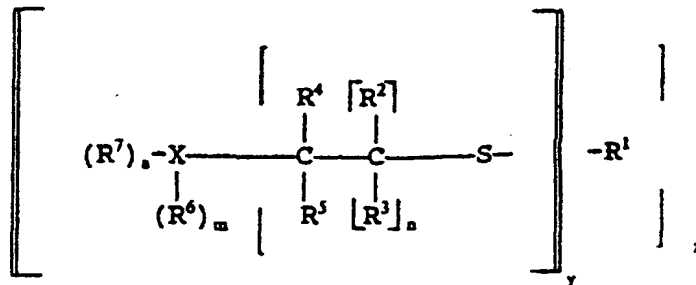
50 32. Zusammensetzung nach Anspruch 30, worin der Mercaptidrest des metallorganischen Mercaptoestersulfids ein Mercaptoalkylcarboxylat ist.

55 33. Polymerzusammensetzung mit einem blockierten Mercaptan der Struktur:



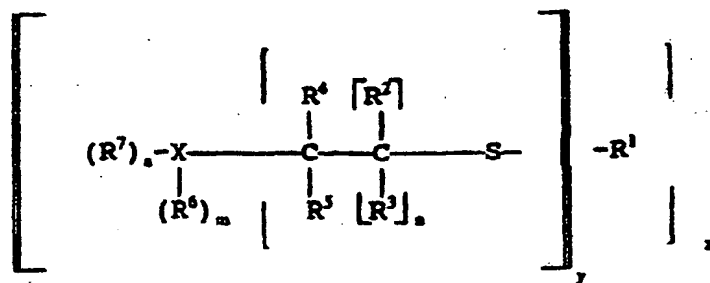
worin a 0 oder 1 ist, m und n 0 oder 1 sind, y 1 bis 4 ist, z 1 bis 4 ist, wenn y 1 ist, und z 1 ist, wenn y mehr als 1 ist, R<sup>1</sup> eine Tetrahydropyranyloxyethylgruppe oder eine Hydroxyalkyl-, Acyloxyalkyl-, Carboxyalkyl- oder Carboxyarylgruppe mit 1 bis 22 Kohlenstoffatomen ist, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> und R<sup>7</sup> unabhängig voneinander Wasserstoff, eine Hydroxyl- oder Mercaptogruppe oder eine Alkyl-, Alkylenyl-, Aryl-, Halogenaryl-, Alkaryl-, Aralkyl-, Hydroxyalkyl-, Mercaptoalkyl-, Hydroxyaryl-, Alkoxyhydroxyaryl-, Mercaptoaryl- oder Acylgruppe mit 1 bis 22 Kohlenstoffatomen sind, X Arylcycloalkyl oder ein Heteroatom ist, wenn a 1 ist, und, wenn a 0 ist, X Aryl, Halogenaryl, Alkaryl, Alkoxyaryl, Arylcycloalkyl oder ein Heteroatom ist, wobei, wenn a 1 ist und m 0 ist, eine der Gruppen R<sup>1</sup>, R<sup>3</sup> oder R<sup>5</sup> mit R<sup>7</sup> und X unter Bildung eines heterozyklischen Restes mit X als Heteroatom Sauerstoff oder Schwefel verbunden sein kann, und wenn a 1 ist und m 1 ist, R<sup>6</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X als ein Stickstoffatom bilden können.

#### 34. Blockiertes Mercaptan der Struktur



worin a 0 oder 1 ist, m und n 0 oder 1 sind, y 1 bis 4 ist, z 1 bis 4 ist, wenn y 1 ist, und z 1 ist, wenn y mehr als 1 ist, R<sup>1</sup> eine Tetrahydropyranyloxyethylgruppe oder eine Hydroxyalkyl-, Carboxyalkyl-, Carboxyaryl- oder Acyloxyalkylgruppe mit 1 bis 22 Kohlenstoffatomen ist, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> und R<sup>7</sup> unabhängig voneinander Wasserstoff, eine Hydroxyl- oder Mercaptogruppe oder eine Alkyl-, Alkylenyl-, Aryl-, Halogenaryl-, Alkaryl-, Aralkyl-, Hydroxyalkyl-, Mercaptoalkyl-, Hydroxyaryl-, Alkoxyhydroxyaryl-, Mercaptoaryl- oder Acylgruppe mit 1 bis 22 Kohlenstoffatomen sind und X ein Heteroatom Sauerstoff, Stickstoff oder Schwefel ist, wobei, wenn a 1 ist und m 0 ist, eine der Gruppen R<sup>1</sup>, R<sup>3</sup> oder R<sup>5</sup> mit R<sup>7</sup> und X unter Bildung eines heterozyklischen Restes mit X als Heteroatom Sauerstoff oder Schwefel verbunden sein kann, und wenn a 1 ist und m 1 ist, R<sup>6</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X als Stickstoffatom bilden können.

#### 35. Zusammensetzung zur Stabilisierung von PVC, im wesentlichen bestehend aus einem Stabilisator auf metallischer Basis für PVC und einem latenten Mercaptan der Formel

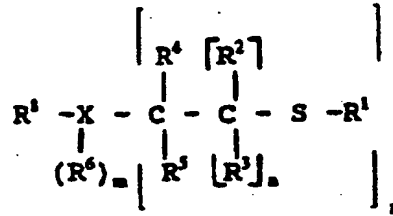


worin a 0 oder 1 ist, m und n 0 oder 1 sind, y 1 bis 4 ist, z 1 bis 4 ist, wenn y 1 ist, und z 1 ist, wenn y mehr als 1 ist, R<sup>1</sup> eine Tetrahydropyranyloxyethylgruppe oder eine Hydroxyalkyl-, Carboxyalkyl- oder Acyloxyalkylgruppe mit 1 bis 22 Kohlenstoffatomen ist, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> und R<sup>7</sup> unabhängig voneinander Wasserstoff, eine Hydroxyl- oder Mercaptogruppe oder eine Alkyl-, Alkylenyl-, Aryl-, Halogenaryl-, Alkaryl-, Aralkyl-, Hydroxyalkyl-, Mercaptoalkyl-, Hydroxyaryl-, Alkoxyhydroxyaryl-, Mercaptoaryl- oder Acylgruppe mit 1 bis 22 Kohlenstoffatomen sind, X Aryl, Halogenaryl, Alkaryl, Aralkaryl, Alkoxyaryl, Arylcycloalkyl oder ein Heteroatom ist, wobei, wenn a 1 ist, eine der Gruppen R<sup>1</sup>, R<sup>3</sup> oder R<sup>5</sup> mit R<sup>7</sup> und X unter Bildung eines heterozyklischen Restes mit X als ein Heteroatom Sauerstoff oder Schwefel verbunden sein können, und wenn m 1 ist, R<sup>6</sup> und R<sup>7</sup> einen heterozyklischen Rest in Verbindung mit X als ein Stickstoffatom bilden können, wobei weiterhin, wenn X Aralkaryl ist, R<sup>6</sup> und R<sup>7</sup> Hydroxyl sind, a 1 ist und m 1 ist, z 1 oder 2 ist, und wobei schließlich, wenn R<sup>6</sup> Hydroxyl oder Mercapto ist, z 1 ist.

36. Zusammensetzung, die ein halogenhaltiges Polymer gegen durch Hitze verursachte Verschlechterung stabilisieren kann, mit einem Wärmestabilisator, wobei dieser Wärmestabilisator das blockierte Mercaptan nach Anspruch 34 ist.
37. Verfahren zur Herstellung eines Wärmestabilisators für halogenhaltige Polymere, bei dem man ein para-substituiertes Phenol mit Formaldehyd in Gegenwart eines Alkalimetallhydroxids in wäßriger Lösung bei einer Temperatur bis zu 60°C kondensiert, wobei das Verhältnis des Phenols zu Formaldehyd bei 1 : 1 bis 1 : 1,05 auf einer Äquivalentgewichtsbasis liegt und das Molverhältnis des Phenols zu Alkalimetallhydroxid etwa 1 : 1 beträgt, die Kondensation durch Kühlen des Reaktionsgemisches unter 20°C abschreckt, das Gemisch neutralisiert, das resultierende Kondensat isoliert und das resultierende Kondensat ohne weitere Reinigung mit einer mercaptanhaltigen Verbindung, die unter Alkylmercaptanen, Mercaptoestern, Mercaptoalkoholen und Mercaptosäuren ausgewählt ist, weiter bei 40°C bis 120°C in Gegenwart eines Säurekatalysators kondensiert.
38. Verfahren nach Anspruch 35, bei dem die Maximaltemperatur während der Phenol/Formaldehyd-Kondensation 50°C beträgt.
39. Verfahren nach Anspruch 35, bei dem die Temperatur während der Phenol/Formaldehyd-Kondensation 35°C bis 50°C beträgt.
40. Verfahren nach den Ansprüchen 35 bis 37, bei dem die Gesamtkonzentration an phenolischen und Formaldehyd-Reaktionspartnern 25 bis 50 Gew.-% beträgt.
41. Verbindung der allgemeinen Formel



worin A Sn, Ba, Ca, Al, Monoalkylzinn, Dialkylzinn oder Trialkylzinn ist, b 1 bis 4 ist und B die allgemeine Formel



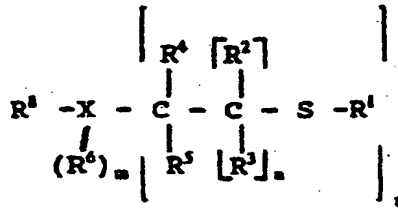
hat, worin m und n 0 oder 1 sind, X Aryl, Alkaryl oder Halogenaryl ist, R<sup>6</sup> O<sup>-</sup> oder S<sup>-</sup> ist, z 1 oder 2 ist und R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> und R<sup>6</sup> wie in Formel 1 in Anspruch 1 definiert sind.

42. Verbindung nach Anspruch 41, worin A Dibutylzinn ist, m 1 ist, n 0 ist, z 1 ist, X Phenyl ist, R<sup>4</sup> und R<sup>5</sup> Wasserstoff sind, R<sup>6</sup> O<sup>-</sup> ist, R<sup>1</sup> Hydroxyethyl ist und b 2 ist.

43. Verbindung der allgemeinen Formel

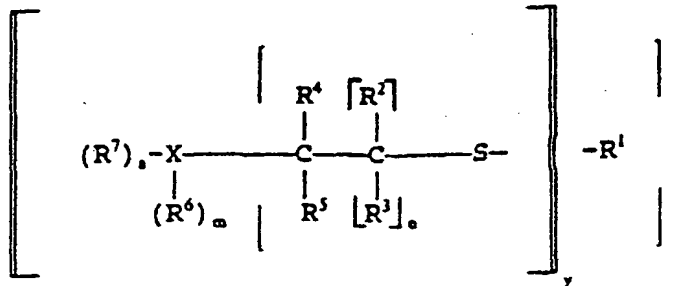


worin P Phosphor ist, Q ein Alkoxy-, Aryloxy-, Aralkoxy-, Alkaryl- oder Halogenarylrest ist, p 1 oder 2 ist und B die allgemeine Formel



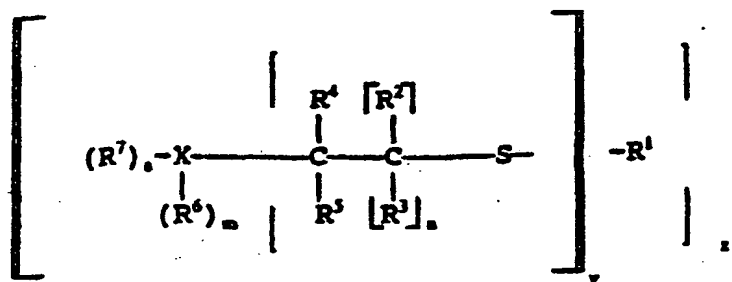
hat, worin m und n 0 oder 1 sind, z 1 oder 2 ist, R<sup>1</sup> eine Alkyl-, Alkyl-, Cycloalkyl-, Cycloalkoxyl-, Aryl-, Alkaryl-, Aralkyl-, Hydroxyalkyl-, Mercaptoalkyl-, Mercaptoalkoxycarbonylalkyl-, Hydroxyaryl-, Mercaptoaryl-, Carboxyalkyl-, Carboxyaryl- oder Acylgruppe mit 1 bis 22 Kohlenstoffatomen ist, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> und R<sup>6</sup> Wasserstoff, eine Hydroxyl-, Mercapto-, Alkyl-, Alkyl-, Aryl-, Halogenaryl-, Alkaryl-, Aralkyl-, Hydroxyalkyl-, Mercaptoalkyl-, Hydroxyaryl-, Alkoxy-(hydroxyaryl) oder Mercaptoarylgruppe mit 1 bis 22 Kohlenstoffatomen sind, X Aryl, Halogenaryl oder Aryl-cycloalkyl ist und R<sup>6</sup> O<sup>-</sup> ist.

44. Polymerzusammensetzung mit einem Polymer, das normalerweise für wärmeinduzierte Verschlechterung durch Autoxidation empfänglich ist, und einem Antioxidationsmittel, welches ein blockiertes Mercaptan der Struktur



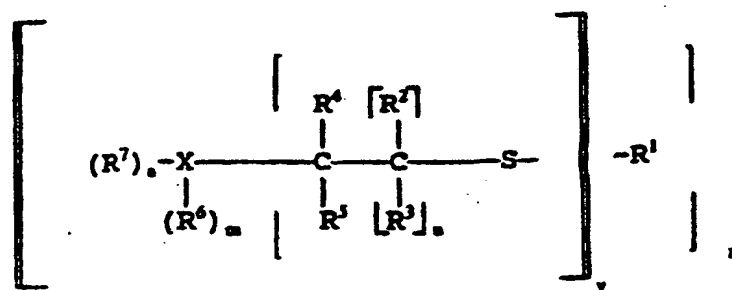
ist, worin a 1 ist, m und n 0 sind, y und z 1 sind, X Phenyl ist, R<sup>4</sup> und R<sup>5</sup> Wasserstoff sind, R<sup>7</sup> o-Hydroxy ist und R<sup>1</sup> Hydroxyethyl ist.

45. Polymerzusammensetzung mit einem Polymer, das normalerweise für wärmeinduzierte Verschlechterung durch Autoxidation empfänglich ist, und einem Antioxidationsmittel, welches ein blockiertes Mercaptan der Struktur



ist, worin a 1 ist, m und n 0 sind, y 1 ist, z 2 ist, X Phenyl ist, R<sup>4</sup> Wasserstoff ist, R<sup>5</sup> Ethyl ist, R<sup>7</sup> o-Hydroxy ist und R<sup>1</sup> Hydroxyethyl ist.

46. Polymerzusammensetzung mit einem halogenhaltigen Polymer, einem ein primäres Mercaptan enthaltenden Wärmestabilisator und geruchmaskierendem latentem Mercaptan der Struktur



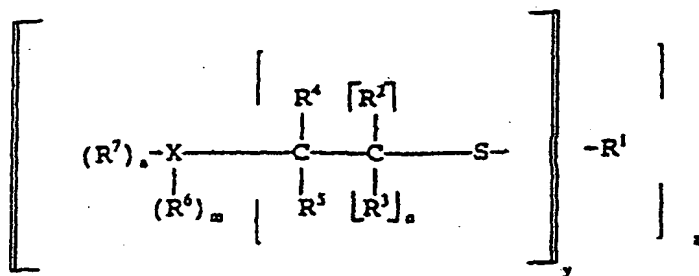
worin a 1 ist, m und n 0 sind, y 1 ist, z 1 ist, R<sup>1</sup> Hydroxyalkyl ist, R<sup>4</sup> Wasserstoff ist, R<sup>5</sup> Wasserstoff oder Alkyl ist, R<sup>7</sup> p-Hydroxy ist und X m-Methoxyphenyl ist.

#### Revendications

1. Une composition englobant un polymère contenant des halogènes et des produits de dégradation d'un mercaptan bloqué présent pendant la transformation de la composition à une température élevée, lesdits produits englobant un mercaptan libre et ledit mercaptan bloqué ayant la structure :

FORMULE

1

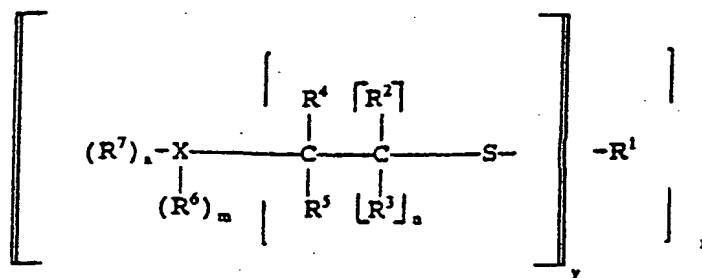


dans laquelle a est 0 ou 1, m et n sont 0 ou 1 ; y = 1 à 4, z est 1 à 4 lorsque y = 1 et z est 1 lorsque y est plus de 1 ; R<sup>1</sup> est un groupe tétrahydropyranyloxyéthyle ou un groupe hydroxyalkyle, acyloxyalkyle, carboxyalkyle ou carboxyaryle ayant de 1 à 22 atomes de carbone ; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> et R<sup>7</sup> peuvent chacun représenter indépendamment l'hydrogène, un groupe hydroxyle ou mercapto ou un groupe alkyle, alkylényle, aryle, haloaryle, alkaryle, aralkyle, hydroxyalkyle, mercaptoalkyle, hydroxyaryle, alkoxyhydroxyaryle, mercaptoaryle ou acyle ayant de 1 à 22 atomes de carbone. X est aryle, haloaryle, alkaryle, aralkyle, alkoxyaryle, arylcycloalkyle, ou un hétéroatome, à condition que, lorsque a est 1 et m est 0, l'un des groupes R<sup>1</sup>, R<sup>3</sup> ou R<sup>5</sup> peut se joindre à R<sup>7</sup> et X pour former une partie hétérocyclique avec X comme hétéroatome d'oxygène ou de soufre, et lorsque a est 1 et m est 1, R<sup>6</sup> et R<sup>7</sup> peuvent former une partie hétérocyclique conjointement avec X comme atome d'azote, à condition que, de plus, lorsque x est aralkyle, R<sup>6</sup> et R<sup>7</sup> sont hydroxyles, a est 1 et m est 1, z est alors 1 ou 2, et à encore une autre condition que, lorsque R<sup>6</sup> ≠ hydroxyle ou mercapto, z est 1.

2. Une composition selon la revendication 1, dans laquelle R<sup>1</sup> est acyloxyalkyle.
3. Une composition selon la revendication 1, dans laquelle R<sup>1</sup> est hydroxyalkyle.
4. Une composition selon la revendication 3, dans laquelle R<sup>1</sup> est hydroxyéthyle.
5. Une composition selon la revendication 3 ou la revendication 4, dans laquelle X est l'azote, m est 1, R<sup>6</sup> est acyle, R<sup>1</sup> est alkyle et n est 0.
6. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est l'azote, m est 1, R<sup>6</sup> et R<sup>7</sup> forment une partie hétérocyclique conjointement avec X, et n est 0.
7. Une composition selon l'une quelconque des revendications 1 à 5, dans laquelle X est l'oxygène, m est 0, R<sup>5</sup> et R<sup>7</sup> forment une partie hétérocyclique conjointement avec X, et n est 0.
8. Une composition selon l'une quelconque des revendications 1 à 6, dans laquelle X est l'oxygène, m est 0, R<sup>5</sup> et R<sup>7</sup> forment une partie hétérocyclique conjointement avec X, et n est 1.
9. Une composition selon l'une quelconque des revendications 1 à 6, dans laquelle X est l'oxygène, R<sup>7</sup> est phényle, m est 0 et n est 1.
10. Une composition selon l'une quelconque des revendications 1 à 6, dans laquelle X est l'oxygène, m est 0, n est 1, R<sup>5</sup> est aryloxyalkyle et R<sup>7</sup> est l'hydrogène.
11. Une composition selon l'une quelconque des revendications 1 à 6, dans laquelle X est l'oxygène, m est 0, n est 1, R<sup>5</sup> est alkoxyalkyle et R<sup>7</sup> est l'hydrogène.
12. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est l'oxygène, m est 0, R<sup>7</sup> et R<sup>1</sup> sont des groupes méthyléniques qui se joignent pour former une partie hétérocyclique avec X et l'atome de soufre, et n est 0.
13. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est phényle, m et n sont 0.

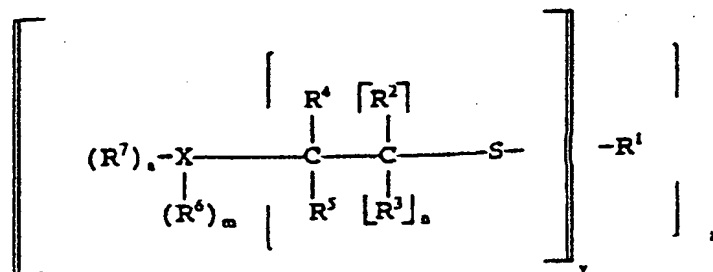
14. Une composition selon la revendication 13, dans laquelle  $R^7$  est hydroxyle.
15. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est phényle,  $R^7$  est hydroxyle, m est 0 et n est 1.
16. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est phénoxy, m est 0 et n est 1.
17. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est benzyle,  $R^7$  est hydroxyle, et m et n sont 0.
18. Une composition selon l'une quelconque des revendications 1 à 4, dans laquelle X est alkoxyphényle,  $R^7$  est hydroxyle et m est 0.
19. Une composition selon l'une quelconque des revendications précédentes, dans laquelle  $R^3$  est alkyle.
20. Une composition selon l'une quelconque des revendications précédentes qui englobe de plus un biocide.
21. Une composition selon la revendication 20 dans laquelle le biocide est 10,10'-oxybisphénoxyarsine (OBPA).
22. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère contenant des halogènes est un polymère chlorure vinylique.
23. Une composition selon l'une quelconque des revendications précédentes, caractérisée de plus par la présence d'un stabilisant thermique à base métallique.
24. Une composition selon la revendication 23, dans laquelle au moins un des stabilisants thermiques à base métallique est sélectionné parmi les stabilisants à base d'antimoine, de baryum, de bore et de calcium, d'étain et de zinc.
25. Une composition selon la revendication 23 ou la revendication 24, dans laquelle le stabilisant thermique à base métallique est un composé organométallique.
26. Une composition selon la revendication 25, dans laquelle le stabilisant thermique à base métallique est un composé d'organotine.
27. Une composition selon la revendication 26, dans laquelle le composé d'organotine est un mercaptide d'organotine.
28. Une composition selon la revendication 27, dans laquelle la partie mercaptide est un thioglycolate alkylique.
29. Une composition selon la revendication 27, dans laquelle la partie mercaptide est un carboxylate mercaptoalkylique.
30. Une composition selon la revendication 25 ou la revendication 26, dans laquelle le stabilisant thermique à base métallique est un sulfure de mercaptoester organométallique.
31. Une composition selon la revendication 30, dans laquelle la partie mercaptide du sulfure de mercaptoester organométallique est un thioglycolate alkylique.
32. Une composition selon la revendication 30, dans laquelle la partie mercaptide du sulfure de mercaptoester organométallique est un carboxylate mercaptoalkylique.
33. Une composition polymère englobant un mercaptan bloqué ayant la structure :





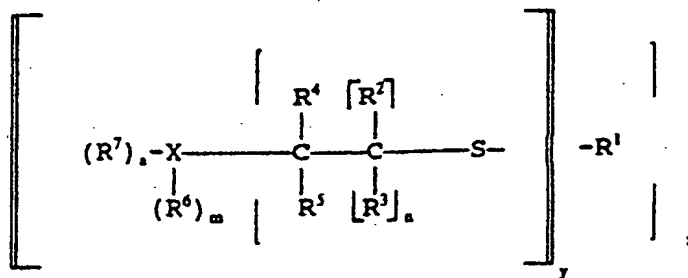
dans laquelle a est 0 ou 1, m et n sont 0 ou 1 ; y = 1 à 4 ; z est 1 à 4 lorsque y = 1 et z est 1 lorsque y est plus de 1 ; R<sup>1</sup> est un groupe tétrahydropyranyloxyéthyle ou un groupe hydroxyalkyle, acyloxyalkyle, carboxyalkyle ou carboxyaryle ayant de 1 à 22 atomes de carbone ; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> et R<sup>7</sup> sont indépendamment l'hydrogène, un groupe hydroxyle ou mercapto ou un groupe alkyle, alkylényle, aryle, haloaryle, alkaryle, aralkyle, hydroxyalkyle, mercaptoalkyle, hydroxyaryle, alkoxyhydroxyaryle, mercaptoaryle ou acyle ayant de 1 à 22 atomes de carbone ; X est arylcycloalkyle ou un hétéroatome lorsque a = 1 et lorsque a = 0, X est aryle, haloaryle, alkaryle, alkoxyaryle, arylcycloalkyle, ou un hétéroatome, à condition que lorsque a est 1 et m est 0, l'un des groupes R<sup>1</sup>, R<sup>3</sup> ou R<sup>5</sup> peut se joindre à R<sup>7</sup> et X pour former une partie hétérocyclique avec X comme un hétéroatome de l'oxygène ou du soufre, et lorsque a est 1 et m est 1, R<sup>6</sup> et R<sup>7</sup> peuvent former une partie hétérocyclique conjointement avec X comme atome d'azote.

34. Un mercaptan bloqué ayant la structure :



dans laquelle a est 0 ou 1, m et n sont 0 ou 1 ; y = 1 à 4, z = 1 à 4 lorsque y = 1 et z est 1 lorsque y est plus de 1 ; R<sup>1</sup> est un groupe tétrahydropyranyloxyéthyle ou un groupe hydroxyalkyle, carboxyalkyle, carboxyaryle ou acyloxyalkyle ayant de 1 à 22 atomes de carbone ; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> et R<sup>7</sup> sont indépendamment l'hydrogène, un groupe hydroxyle ou mercapto ou un groupe alkyle, alkylényle, aryle, haloaryle, alkaryle, aralkyle, hydroxyalkyle, mercaptoalkyle, hydroxyaryle, alkoxyhydroxyaryle, mercaptoaryle ou acyle ayant de 1 à 22 atomes de carbone ; et X est un hétéroatome d'oxygène, d'azote ou de soufre à condition que, lorsque a est 1 et m est 0, l'un des groupes R<sup>1</sup>, R<sup>3</sup> ou R<sup>5</sup> peut se joindre à R<sup>7</sup> et X pour former une partie hétérocyclique avec X comme un hétéroatome d'oxygène ou de soufre, et lorsque a = 1 et m est 1, R<sup>6</sup> et R<sup>7</sup> peuvent former une partie hétérocyclique conjointement avec X comme un atome d'azote.

35. Une composition de stabilisation du PVC englobant essentiellement un stabilisant à base métallique pour le PVC et un mercaptan latent ayant la formule :

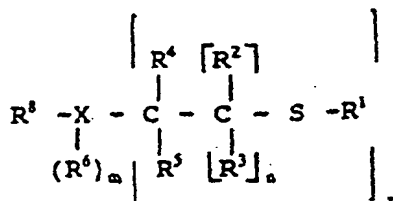


dans laquelle a est 0 ou 1, m et n sont 0 ou 1 ; y = 1 à 4, z = 1 à 4 lorsque y = 1 et z est 1 lorsque y est plus de 1 ; R<sup>1</sup> est un groupe tétrahydropyranyloxyéthyle ou un groupe hydroxyalkyle, carboxyalkyle, carboxyaryle ou acyloxyalkyle ayant de 1 à 22 atomes ; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> et R<sup>7</sup> sont indépendamment l'hydrogène, un groupe hydroxyle ou mercapto ou un groupe alkyle, alkylényle, aryle, haloaryle, alkaryle, aralkyle, hydroxyalkyle, mercaptoalkyle, hydroxyaryle, alkoxyhydroxyaryle, mercaptoaryle ou acyle ayant de 1 à 22 atomes de carbone ; X est aryle, haloaryle, alkaryle, aralkyle, alkoxyaryle, arylcycloalkyle, ou un hétéroatome, à condition que, lorsque a est 1, l'un des groupes R<sup>1</sup>, R<sup>3</sup> ou R<sup>5</sup> peut se joindre à R<sup>7</sup> et X pour former une partie hétérocyclique avec X comme un hétéroatome d'oxygène ou de soufre, et lorsque m est 1, R<sup>6</sup> et R<sup>7</sup> peuvent former une partie hétérocyclique conjointement avec X comme un atome d'azote, à condition, de plus, que lorsque X est aralkyle, R<sup>6</sup> et R<sup>7</sup> sont hydroxyles, a est 1 et m est 1, z est alors 1 ou 2, et à condition, de plus, que lorsque R<sup>6</sup> ≠ hydroxyle ou mercapto, z est 1.

36. Une composition capable de stabiliser un polymère contenant des halogènes contre la détérioration due à la chaleur, ladite composition englobant un stabilisant thermique, ledit stabilisant thermique étant le mercaptan bloqué de la revendication 34.
37. Un procédé de préparation d'un stabilisant thermique pour les polymères contenant des halogènes, ledit procédé englobant la condensation d'un phénol *para*-substitué avec le formaldéhyde en présence d'un hydroxyde de métal alcalin en solution aqueuse à une température maximum de 60°C, le rapport entre le phénol et le formaldéhyde étant de 1:1 à 1:1,05 sur une base de poids équivalent, et le rapport molaire entre le phénol et l'hydroxyde de métal alcalin est voisin de 1:1, ce qui modère la condensation en refroidissant le mélange de réaction au-dessous de 20°C, neutralisation du mélange, isolation du condensat résultant et autre condensation du condensat résultant sans aucune autre purification avec un composé contenant du mercaptan sélectionné parmi les mercaptans alkyles, les mercaptoesters, les mercaptoalcools et les mercaptoacides à 40°C à 120°C en présence d'un catalyseur acide.
38. Un procédé selon la revendication 35, selon lequel la température maximale pendant la condensation phénol/formaldéhyde égale 50°C.
39. Un procédé selon la revendication 35, selon lequel la température pendant la condensation phénol/formaldéhyde égale 35°C à 50°C.
40. Un procédé selon les revendications 35 à 37, selon lequel la concentration totale de réactifs phénolique et formaldéhyde est de 25 à 50% en poids.
41. Un composé ayant la formule générale :



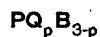
dans laquelle a est Sn, Ba, Ca, Al, monoalkyltine, dialkyltine, trialkyltine, b est de 1 à 4 et B a la formule générale :



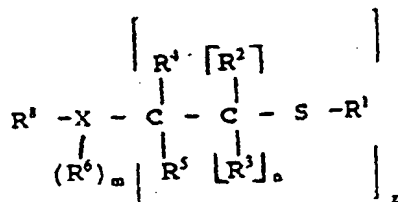
dans laquelle m et n sont 0 ou 1, X est aryle, alkaryle ou haloaryle, R<sup>8</sup> est O<sup>-</sup> ou S<sup>-</sup>, z est 1 ou 2 et R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> et R<sup>6</sup> sont tels que définis relativement à la Formule 1 de la revendication 1.

42. Un composé selon la revendication 41, dans lequel A est dibutyltétain, m = 1, n = 0, z = 1, X est phényle, R<sup>4</sup> et R<sup>5</sup> sont l'hydrogène, R<sup>8</sup> est O<sup>-</sup>, R<sup>1</sup> est hydroxyéthyle et b est 2.

43. Un composé ayant la formule générale :

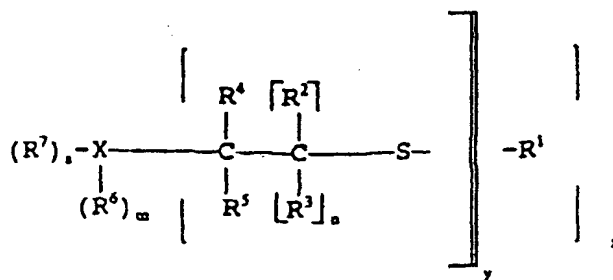


dans laquelle P est le phosphore, Q est un radical alkoxy, aryloxy, aralkoxy, alkaryloxy ou haloaryloxy, p est 1 ou 2 et B a la formule générale :



dans laquelle m et n sont 0 ou 1 ; z est 1 ou 2 ; R<sup>1</sup> est un groupe alkyle, alkylène, cycloalkyle, cycloalkoxy, aryle, alkaryle, aralkyle, hydroxyalkyle, mercaptoalkyle, mercaptoalkoxycarbonylalkyle, hydroxyaryle, mercaptoaryle, carboxyalkyle, carboxyaryle ou acyle ayant de 1 à 22 atomes de carbone ; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> et R<sup>6</sup> sont l'hydrogène, un groupe hydroxyle, mercapto, alkyle, alkylène, aryle, haloaryle, alkaryle, aralkyle, hydroxyalkyle, mercaptoalkyle, hydroxyaryle, alkoxy(hydroxyaryl), ou mercaptoaryle ayant de 1 à 22 atomes de carbone ; X est aryle, haloaryle ou arylcycloalkyle, et R<sup>8</sup> est O<sup>-</sup>.

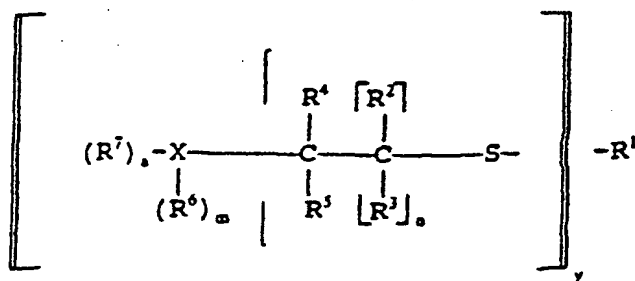
44. Une composition polymérique englobant un polymère normalement susceptible de détérioration due à la chaleur par auto-oxydation et un antioxydant qui est un mercaptan bloqué ayant la structure :



# EP 0 742 259 B1

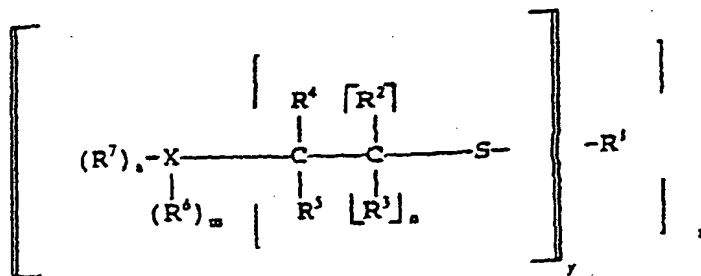
dans laquelle a est 1, m et n sont 0, y et z sont 1, X est phényle, R<sup>4</sup> et R<sup>5</sup> sont l'hydrogène, R<sup>7</sup> est O-hydroxy et R<sup>1</sup> est hydroxyéthyle.

45. Une composition polymérique englobant un polymère normalement susceptible de détérioration due à la chaleur par auto-oxydation et un antioxydant qui est un mercaptan bloqué ayant la structure :



dans laquelle a est 1, m et n sont 0, y est 1, z est 2, X est phényle, R<sup>4</sup> est l'hydrogène, R<sup>5</sup> est éthyle, R<sup>7</sup> est O-hydroxy et R<sup>1</sup> est hydroxyéthyle.

46. Une composition polymérique englobant un polymère contenant des halogènes, un stabilisant thermique primaire contenant du mercaptan et un mercaptan latent masquant les odeurs, ayant la structure :



dans laquelle a est 1, m et n sont 0, y est 1, z est 1, R<sup>1</sup> est hydroxyalkyle, R<sup>4</sup> est l'hydrogène, R<sup>5</sup> est l'hydrogène ou alkyle, R<sup>7</sup> est p-hydroxy et X est m-méthoxyphényle.